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Advances in Polyurethane Dispersions

2021 Coatings Trends and Technologies
Lombard, IL
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Laurie Morris
Senior Chemist

Outline

Introduction
- History
- Chemistry and Morphology
- PUD manufacturing

Properties of Polyurethane Dispersions

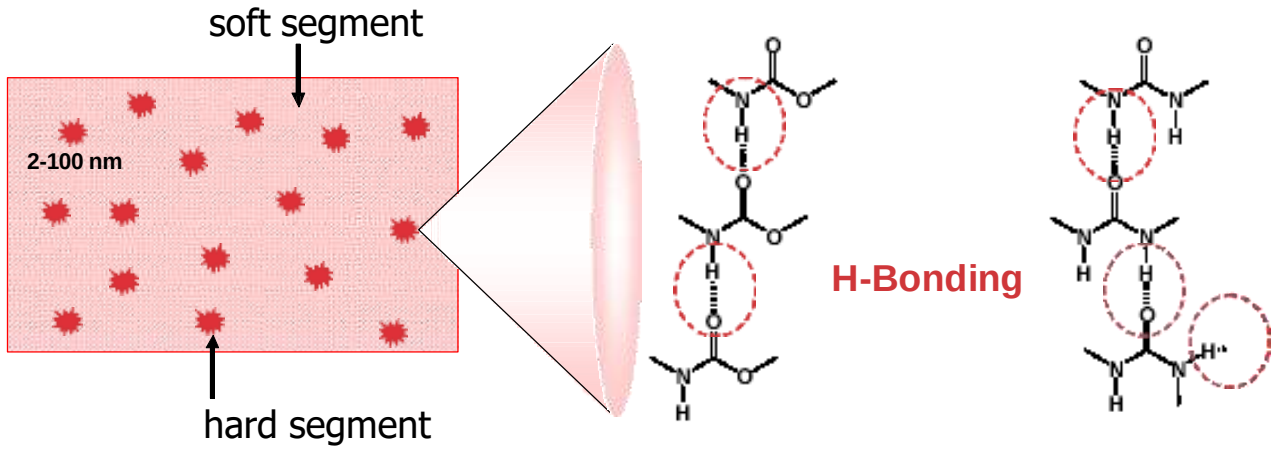
Innovative Technologies

Applications

Conclusions

Introduction: PU History and Morphology

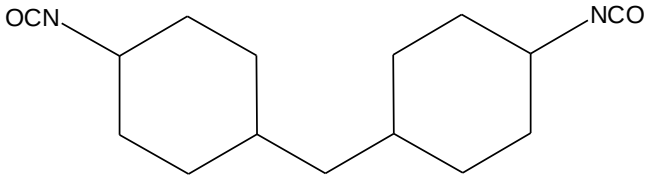
1930	1940s	1950s	1960s	1970s	1980s	1990s
Otto Bayer invented PU ☼ Isocyanate/PUs ☼ Urethane lacquers	☼ Rigid PU foams ☼ Isocyanate/alkyds	☼Flexible PU foam ☼Urethane elastomers ☼Aromatic prepolymers in coatings	☼ Polyisocyanate alkyd enamels	☼ PUDs ☼ RIM	☼ 2-component PUs	☼ 1-K Blocked Iso systems ☼ 2-K WB PU coatings



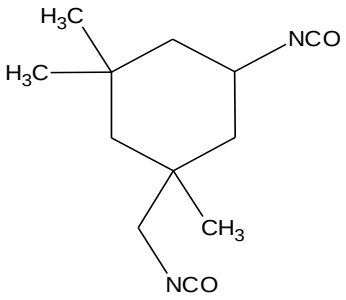
- acts as crosslinking point
- will release under strain
- allows flow to relieve stress
- allows self healing of defects

Traditional PUD Building Blocks for Coatings

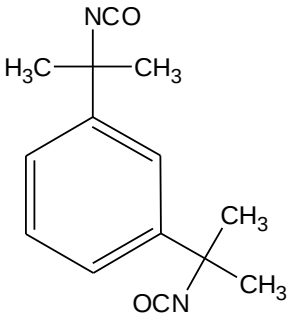
Isocyanates



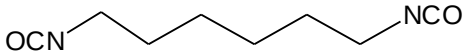
H_{12}MDI



IPDI

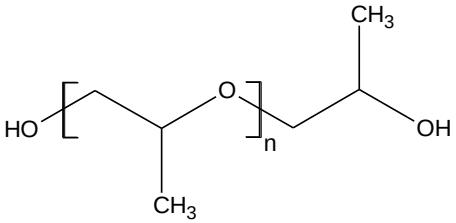


TMXDI

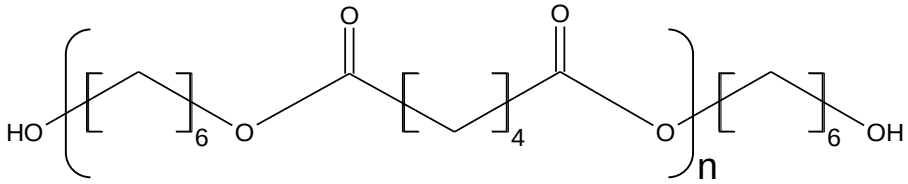


HDI

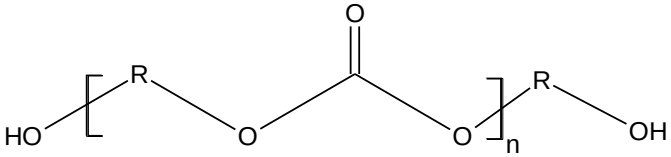
Polyols/Co-reactants



Polyether polyol



Polyester polyol



Polycarbonate polyol

Aqueous Polyurethane Dispersions – Traditional Chemistry

Pre-polymer preparation

A polyol is reacted with a stoichiometric excess of isocyanate to produce a pre-polymer.

Dimethylpropionic acid (DMPA), an anionic stabilizing agent, is used to build functionality into the polymer chain.

Neutralization

An amine, typically TEA or DMEA, is used for neutralization.

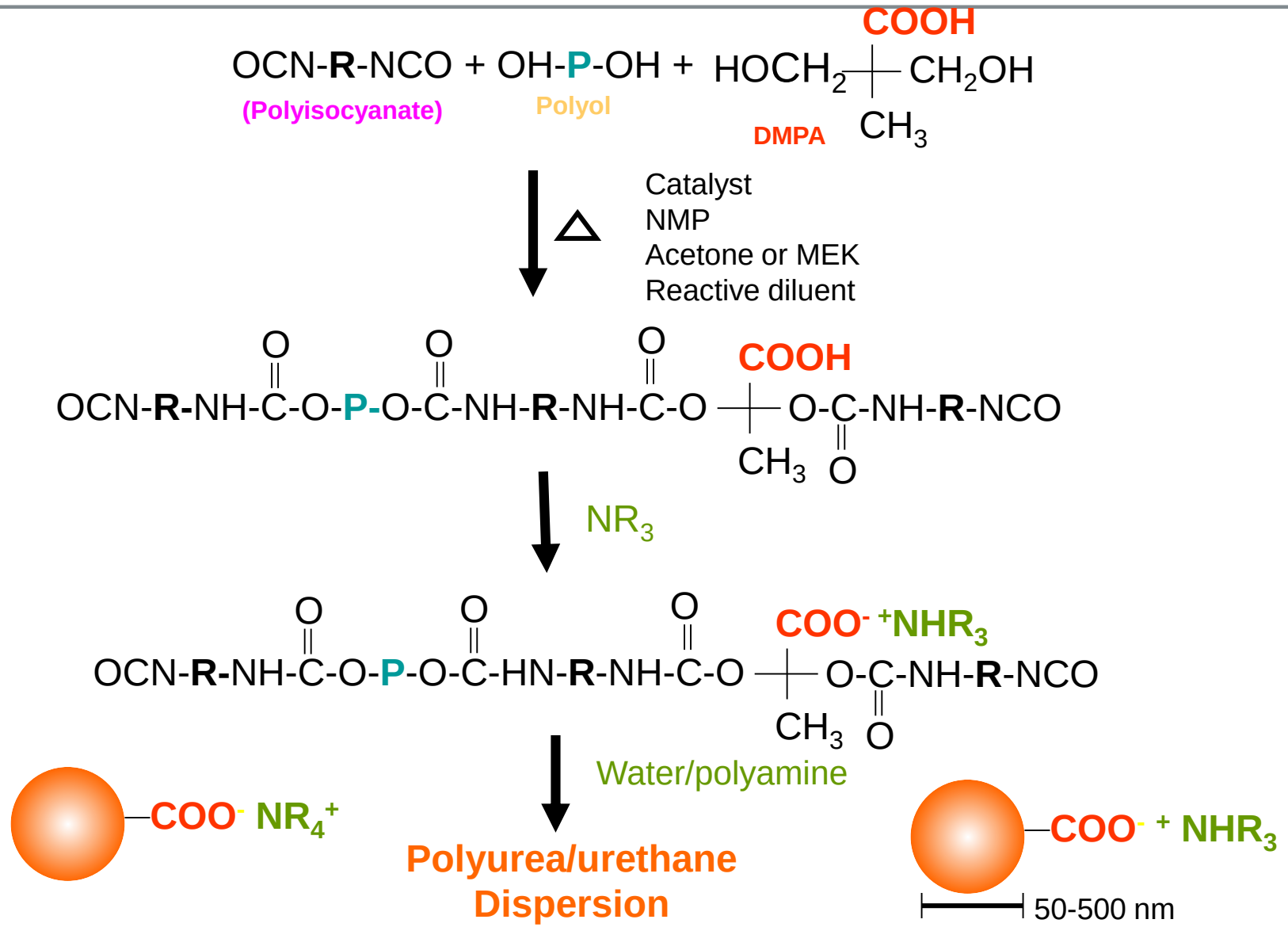
Dispersion

The pre-polymer is dispersed in water.

Chain Extension

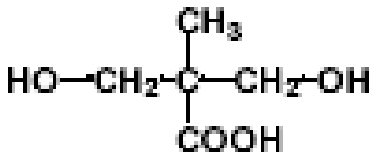
Molecular weight is increased.

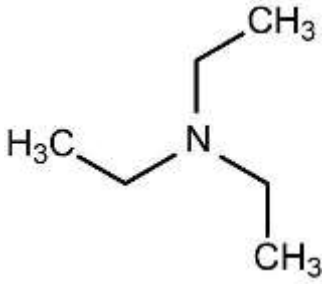
Traditional PUD Chemistry



Ion Bearing Molecules

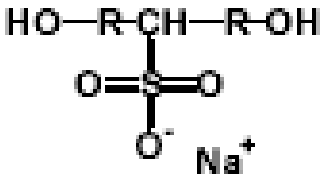
- Dimethyl Propionic acid
  - Typically used with tertiary amines
  - Looses hydrophilicity upon amine evaporation
  - Relatively high Tg component
  - Insoluble in PU component

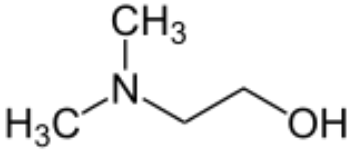




TEA

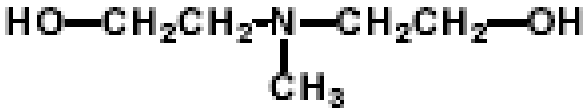
- Sodium Sulfonate Diols
  - Na salt remains in film
  - Relatively low Tg component
  - Improved solution stability of polyesters

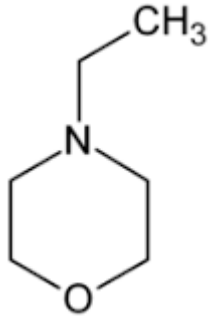




DMEA

- Tertiary amine diol
  - Typically used with HCl or AcCOOH
  - Commonly used for paper and leather application



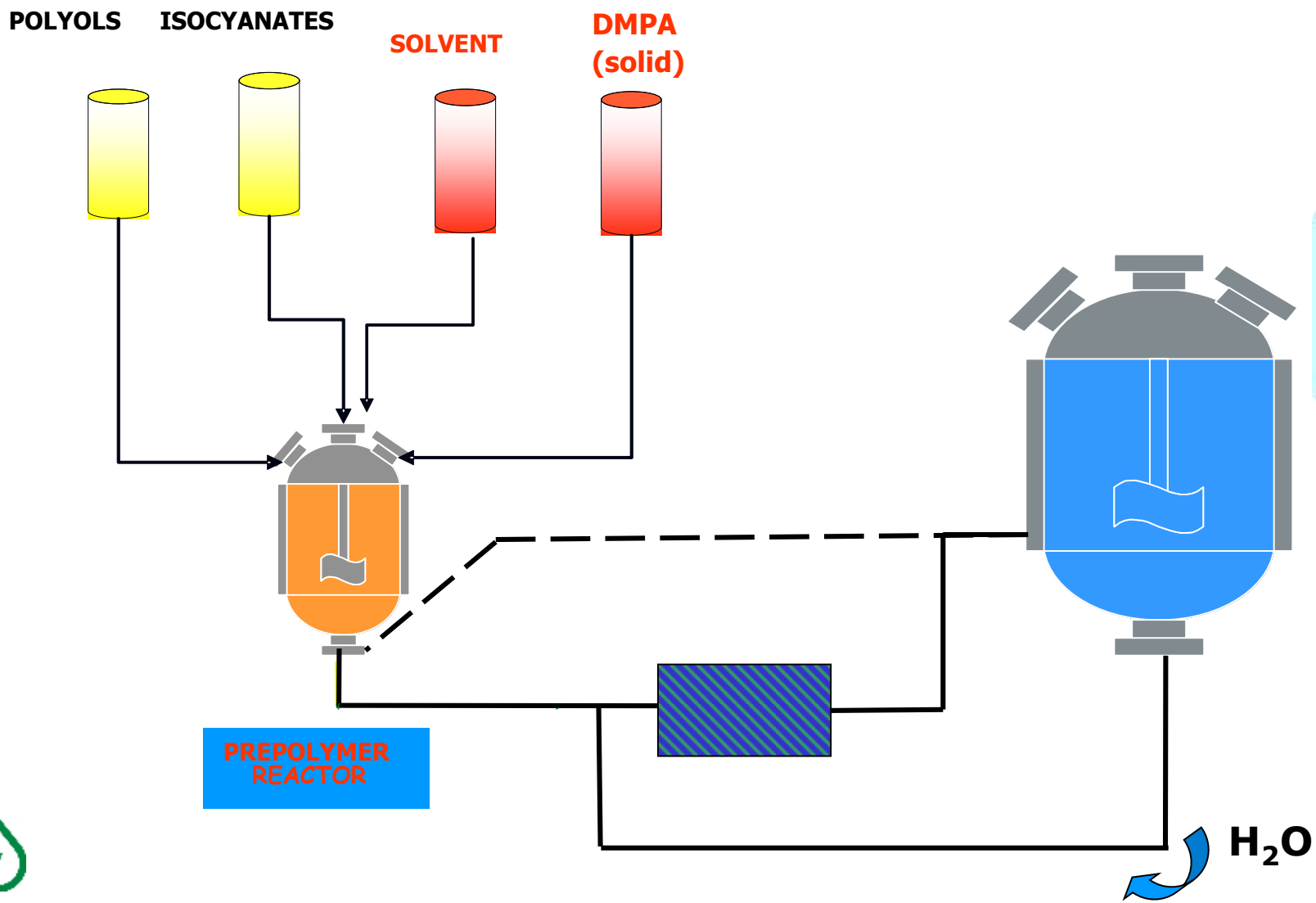


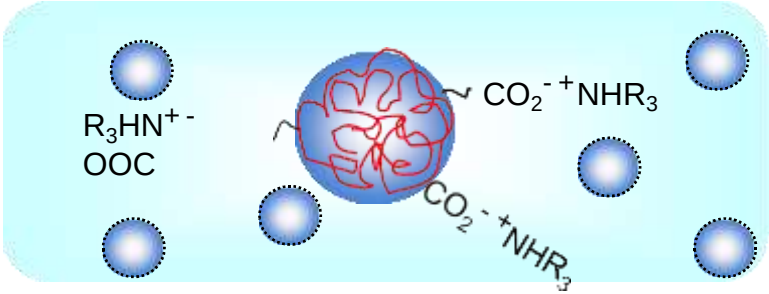
NEM

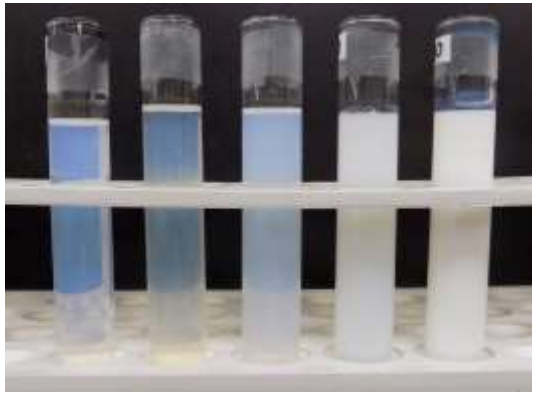
Solvent-free PUDs

- Traditional PUDs were manufactured using N-methyl-2-pyrrolidone (NMP) to reduce the pre-polymer viscosity.
- Environmental restrictions against NMP have lead to the development of solvent-free PUDs.
- Distillation - Acetone or MEK is used to control the pre-polymer viscosity. Then after the chain extension the acetone or MEK is removed.
- Reactive diluent – A reactive diluent, such as an acrylic monomer, is used to control the pre-polymer viscosity and then polymerized.
- Innovations in equipment have lead to dispersing units that can handle much higher viscosity materials.

PUD Manufacturing







Properties of Polyurethane Dispersions

Abrasion Resistance

Flexibility

Scratch and Mar Resistance

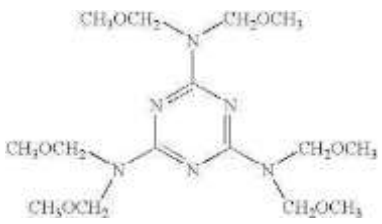
Hardness

Toughness

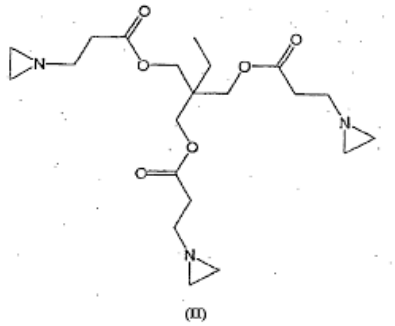
Weatherability

Functionality - Crosslinkable

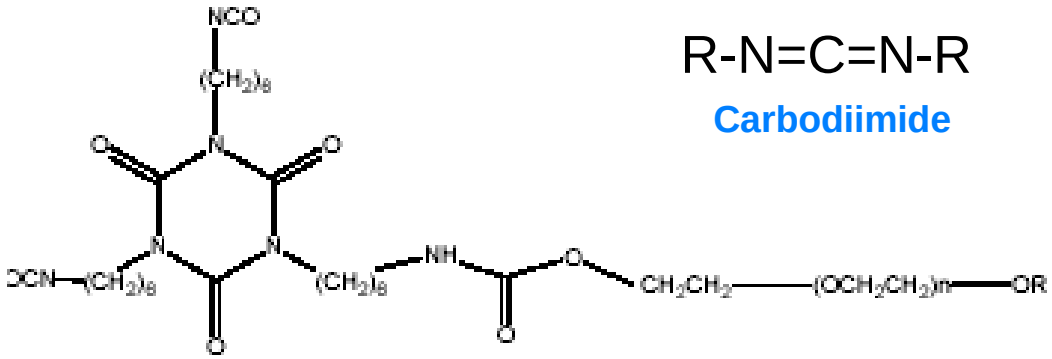
Crosslinking of PUDs: Common Approaches



Melamine formaldehyde



Polyaziridine



Emulsifiable isocyanate

$R\text{-}N{=}C{=}N\text{-}R$

Carbodiimide

$X\text{-}(CH_2)_n\text{-}Si\text{-}(OR)_3$

n: ~3-5

X: NH_2,OH,NCO,epoxy

R: CH_3, C_2H_5, C_3H_7

Functional siloxanes

Innovative Technologies

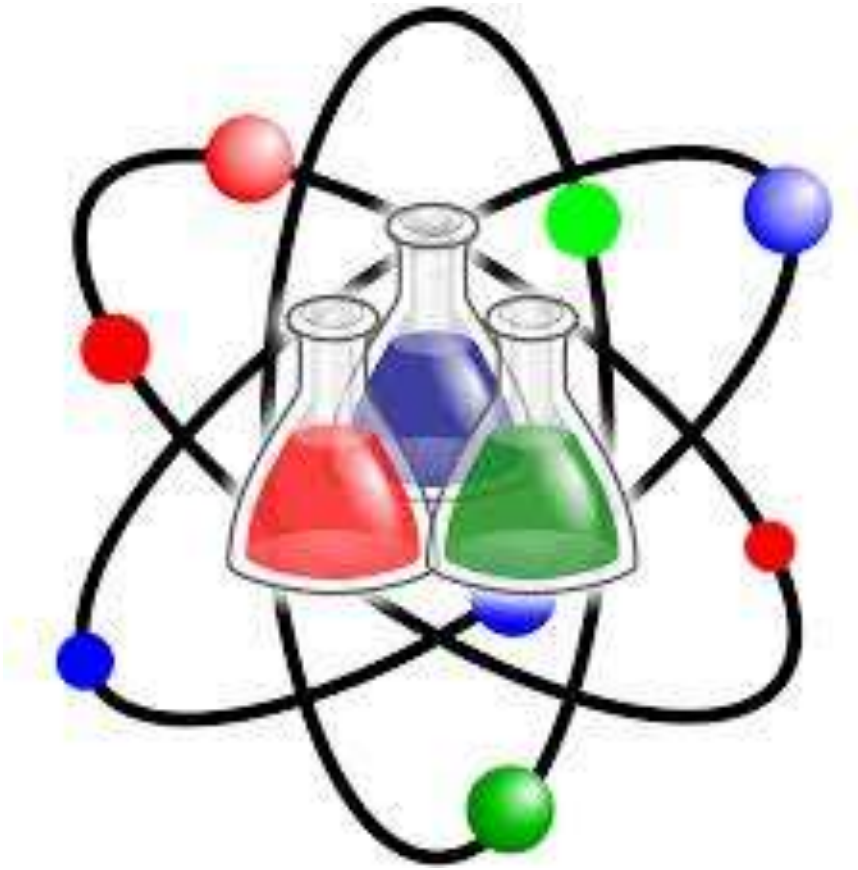
Renewable PUDs

- -Castor Oil
- -Linseed Oil

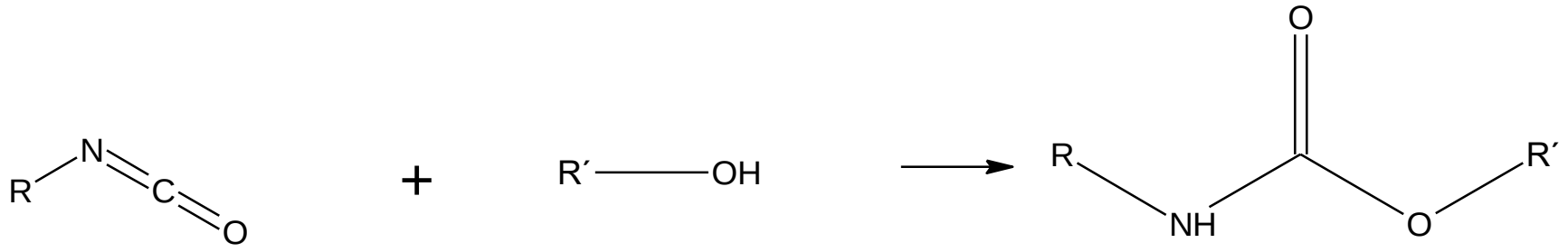
UV Curable PUDs

Amine-free PUDs

Inherently Matte PUDs



Polyurethane Dispersions Based on Renewable Resources



Isocyanate

Polyol based on natural oils

Polyurethane Dispersion

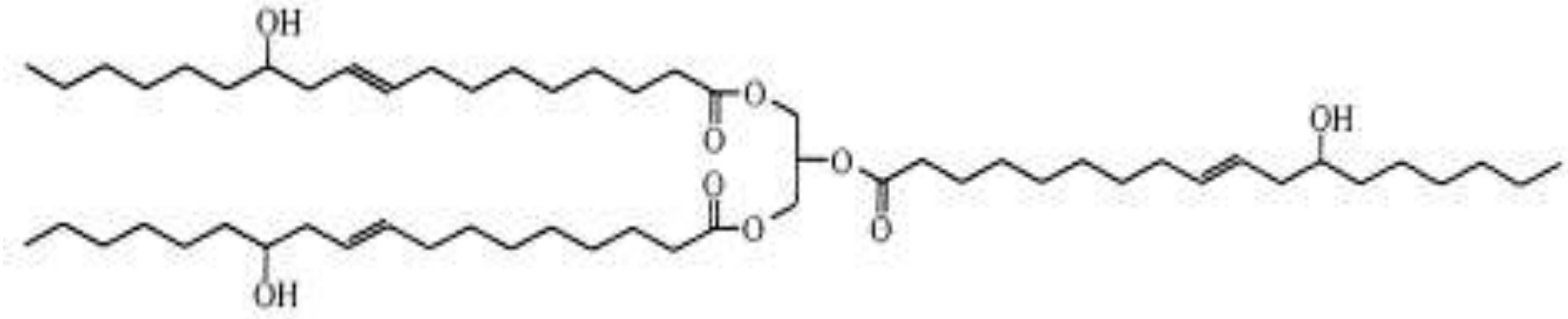
Natural oils extracted from:

- castor beans
- soybeans
- flax seeds
- rapeseeds

Castor Oil

Major component in castor oil, produced via an esterification reaction involving ricinoleic acid.

This fatty acid contains a hydroxyl functionality on the twelfth carbon which allows further chemical modification, specifically reaction with isocyanates to produce polyurethanes.



Polyurethane Dispersions Based on Castor Oil

Used for 1K and 2K Floor Coatings and Furniture Coatings

Excellent abrasion resistance

Outstanding wood warming properties

Excellent black heel mark resistance

Excellent gloss

Used for interior "green" wall paints and hobby adhesives

Very good pigment wetting

Amine-free

Odor and VOC free

Non-yellowing

Conforms to European Toy Regulation EN 71-3

Castor Oil Based PUDs

Available with elongation at break values ranging from 60% to 175%

Available with Koenig Pendulum Hardness values ranging from 85 to 115 seconds

Available with a renewable content ranging from 8% to 40%

Polyurethane Dispersions Based on Linseed Oil

Alternative to solvent-borne urethanes, suitable for parquet-coatings and DIY-lacquers

Solvent-free

Outstanding wood warming properties

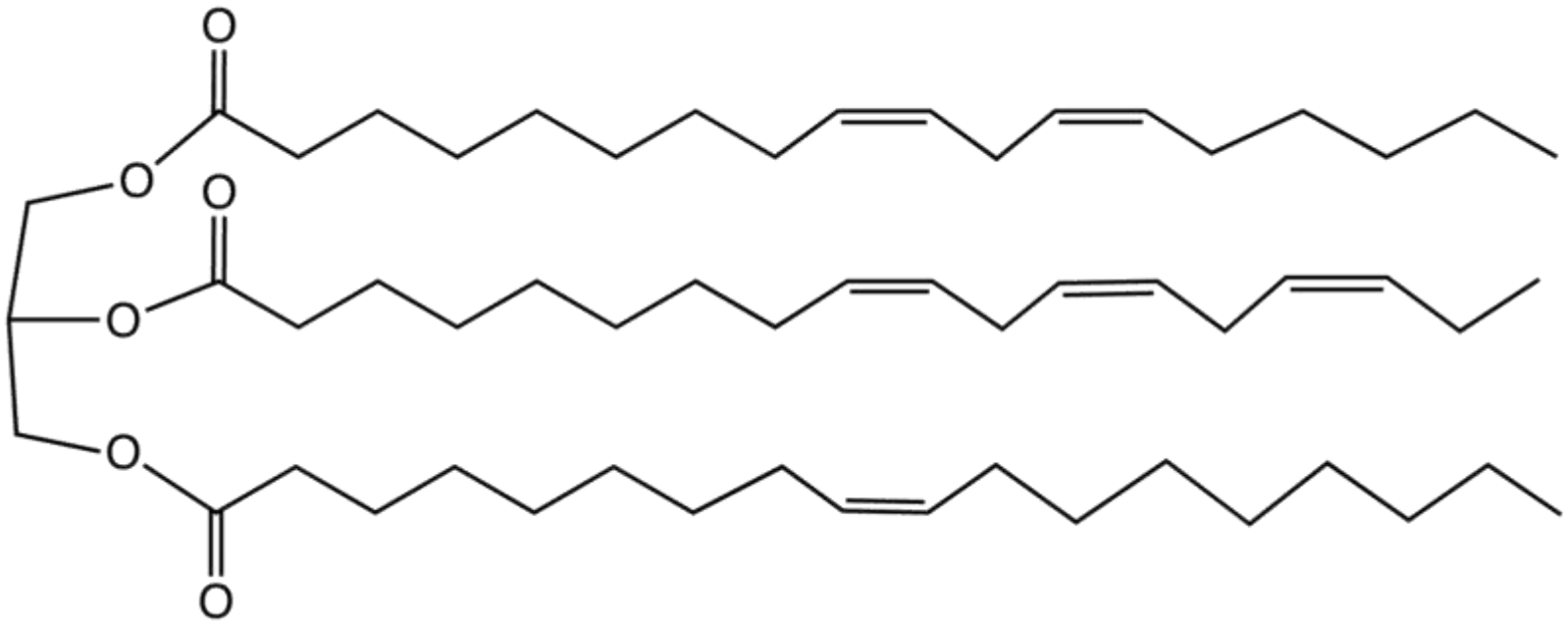
Oxidative drying - faster drying with addition of driers
(e.g. Co, Mn for surface drying and Ba, Zr for through drying)

Excellent exterior durability

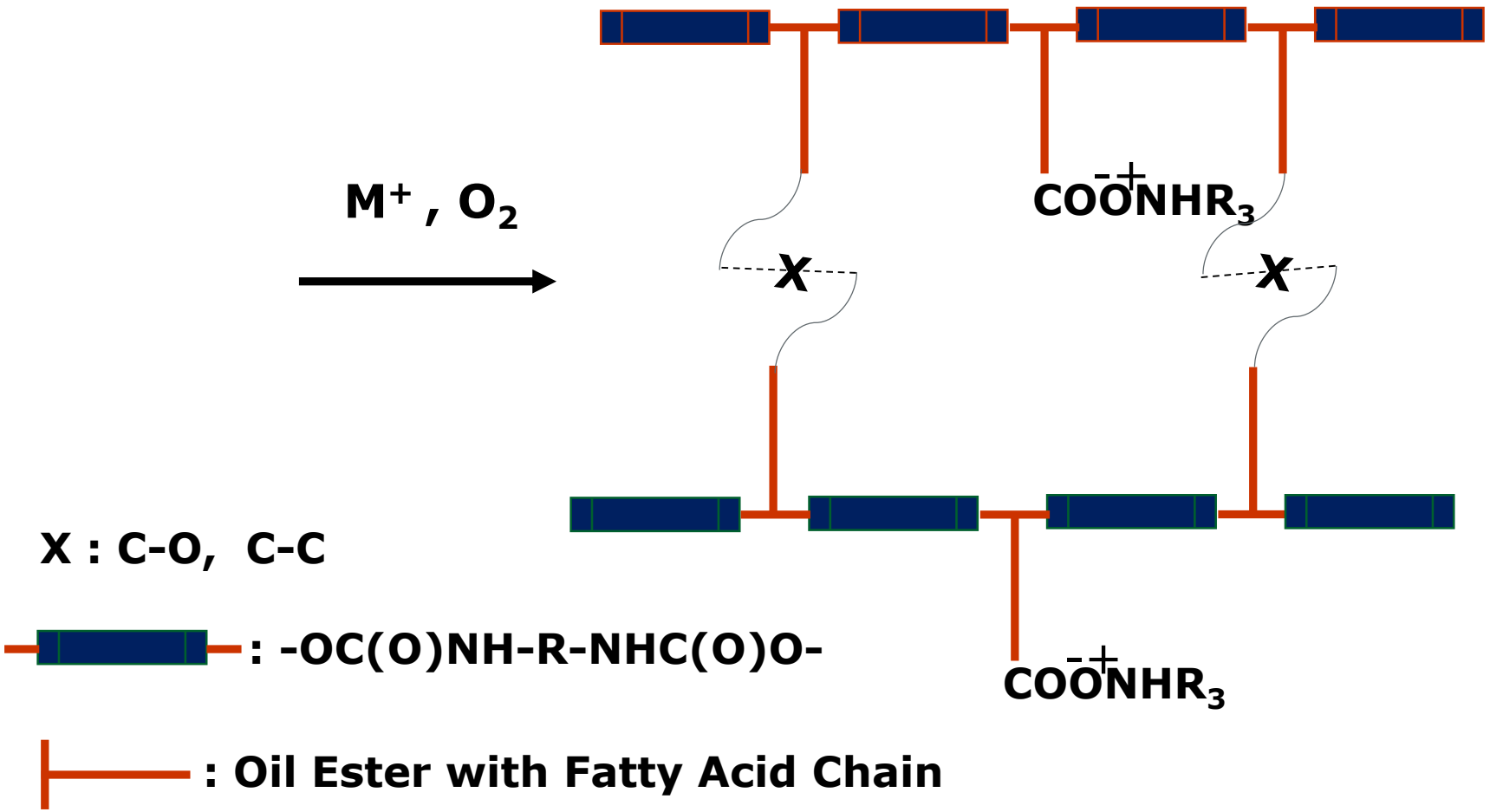
Alkyd-like flow

Flax Plant

Triglyceride found in Linseed Oil, a triester derived from linoleic acid, alpha-linolenic acid, and oleic acid.



Oxidative cure of Linseed Oil based PUDs



Linseed Oil Based PUDs

Application Areas include:

Hardwood floor coatings

DIY lacquers

Furniture coatings

Exterior wood coatings

Wood stains

Linseed Oil Based PUDs

-Contains 30 - 50% renewable content

-Very fast hardness development

-Excellent adhesion

-Solvent-free formulations are possible

-Excellent chemical resistance

-Very good sanding properties

.

Emerging Technologies – Other Renewable PUDs

Rapeseed

Soybean

UV Curable PUDs

Very low VOC

No low molecular weight reactive diluents needed

Excellent grain definition

Excellent atomization and flow

Little to no shrinkage

Excellent block resistance

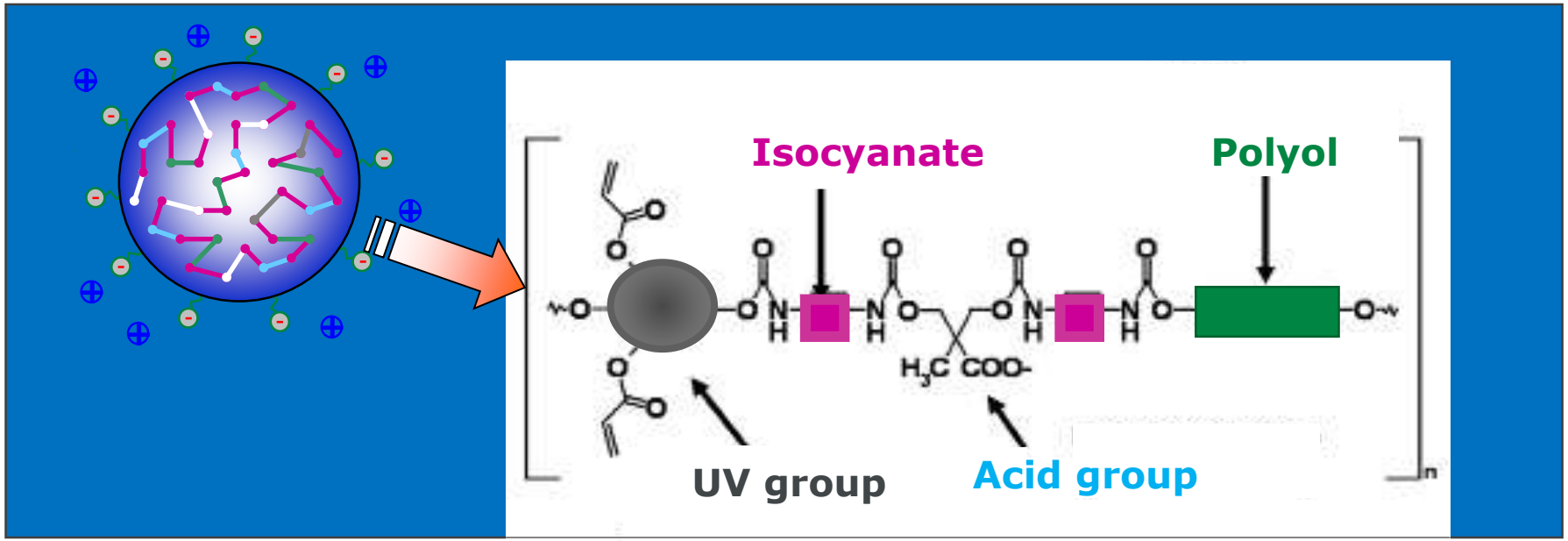
Wide range of application methods

Easy formulating and flattening

Immediate property development

Can be easily formulated to pass KCMA specifications

UV Curable PUDs



- High molecular weight dispersions; lower crosslinking density
  - Low shrinkage
  - Adhesion to multiple substrates
- Excellent chemical resistance
- Excellent mechanical properties
- Multiple polymer design options
- Low MFFT --- Solvent free formulations; no reactive diluent
- Dual cure options

UV Curing Basics

Ultraviolet (UV) curing is a photochemical process where intense UV light is used to cure coating.

Photopolymerization is achieved through a free radical mechanism. A photoinitiator is the "catalyst" for the free radical mechanism.

UV light splits the photoinitiator into free radicals.

The radicals react with the double-bonds of the UV-dispersion

This produces more free radicals and the reaction process continues until terminated

By the use of multifunctional resins, a three dimensional network can be created

Experimental

A traditional UV PUD stabilized with DMPA/tertiary amine has been compared to a similar UV PUD stabilized with Sodium Sulfonate and evaluated for:

Koenig Pendulum Hardness

Dry Time

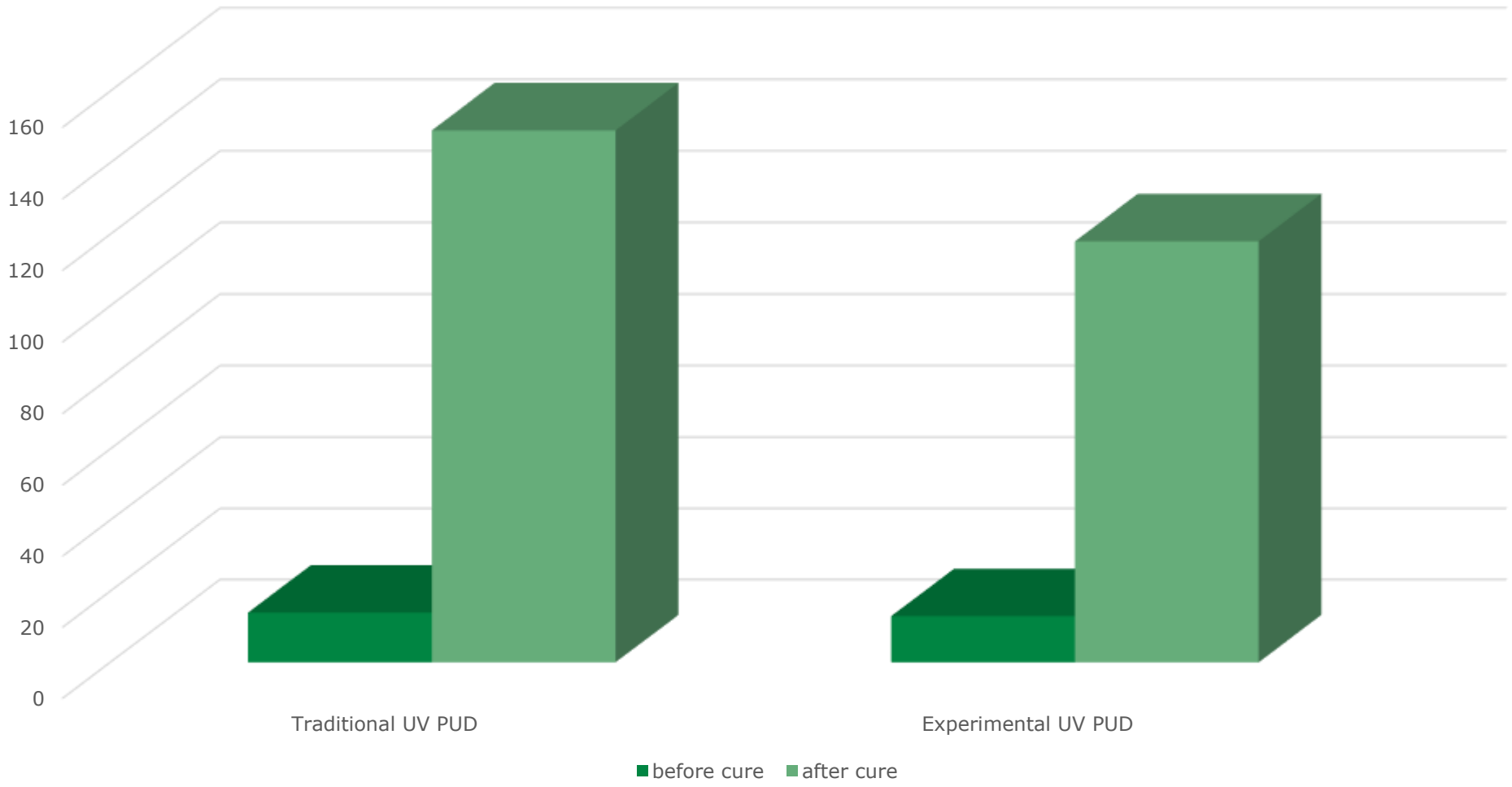
Chemical Resistance

Boiling Water Resistance

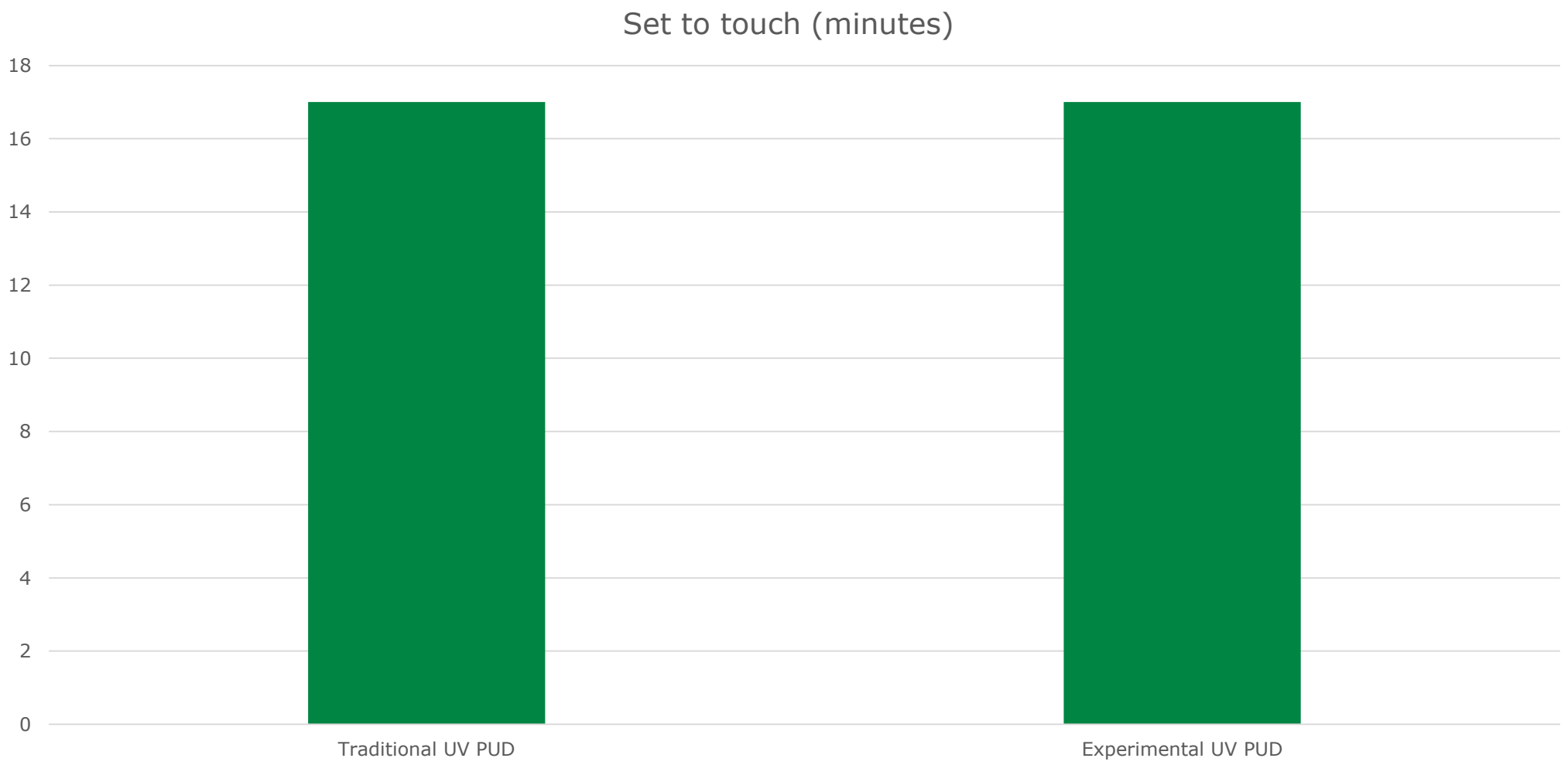
Scratch Resistance

Elevated Temperature Stability (50°C)

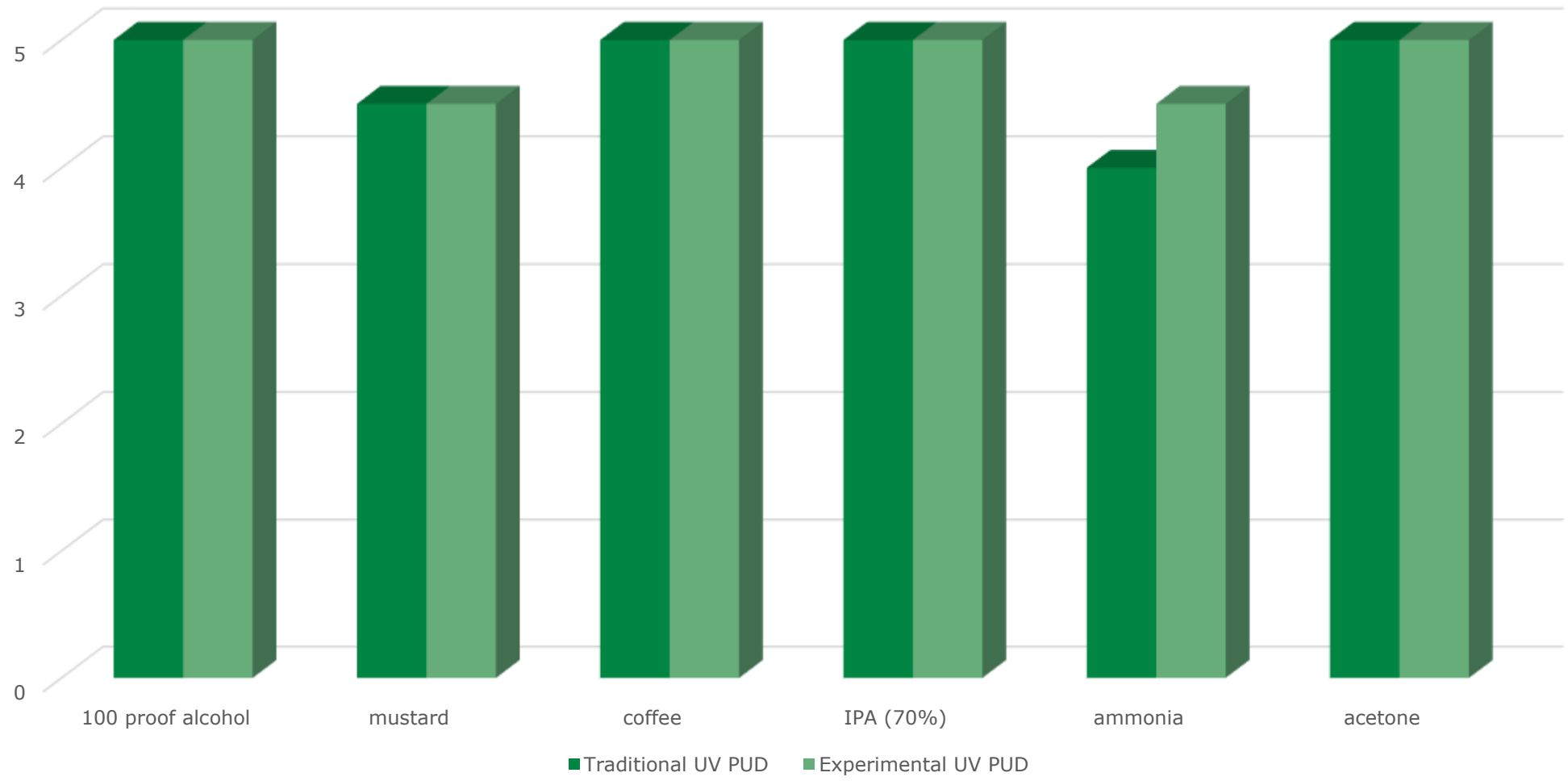
Koenig Pendulum Hardness



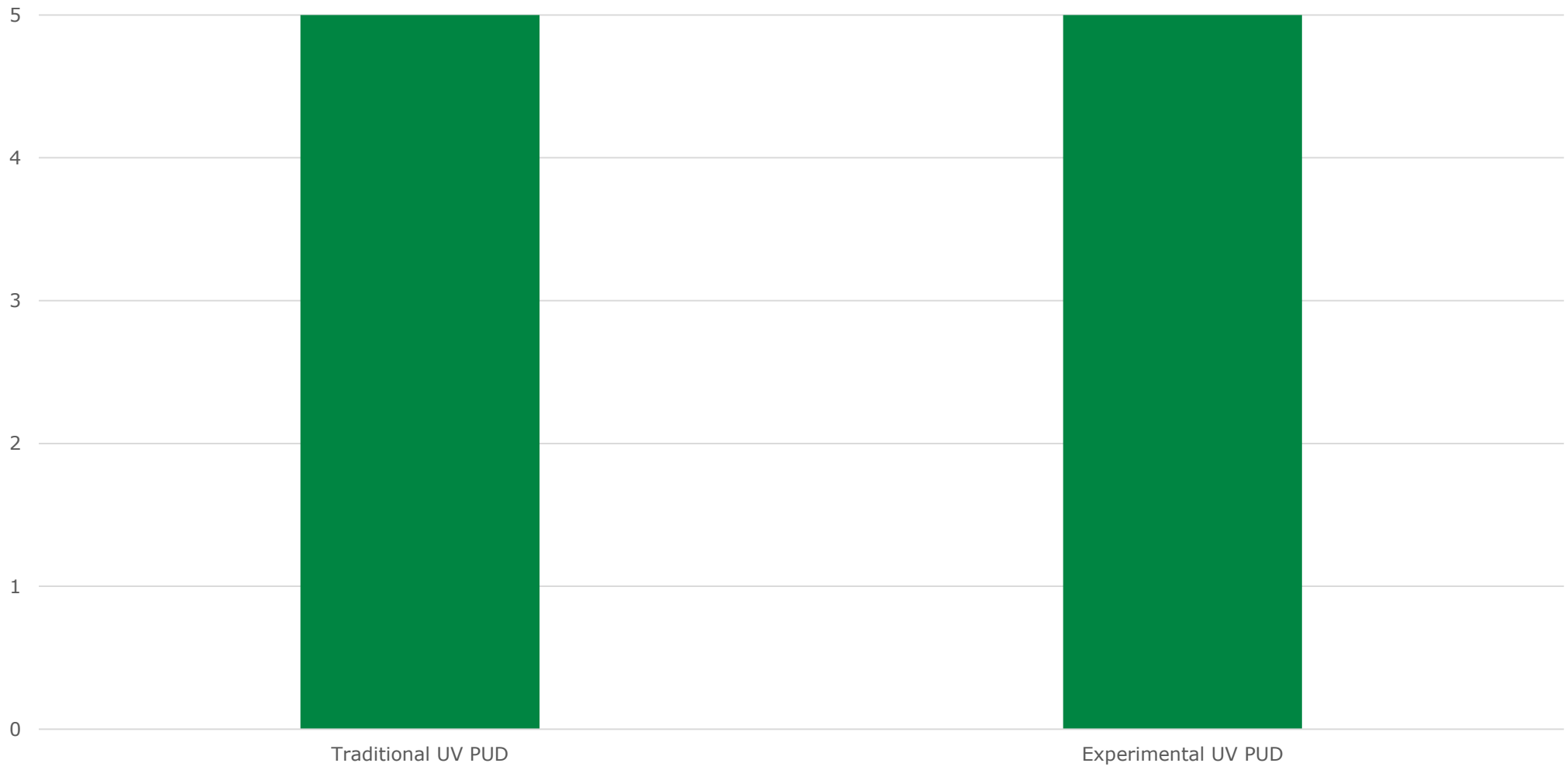
Dry Time


Set to touch (minutes)
18
16
14
12
10
8
6
4
2
0
Traditional UV PUD
Experimental UV PUD

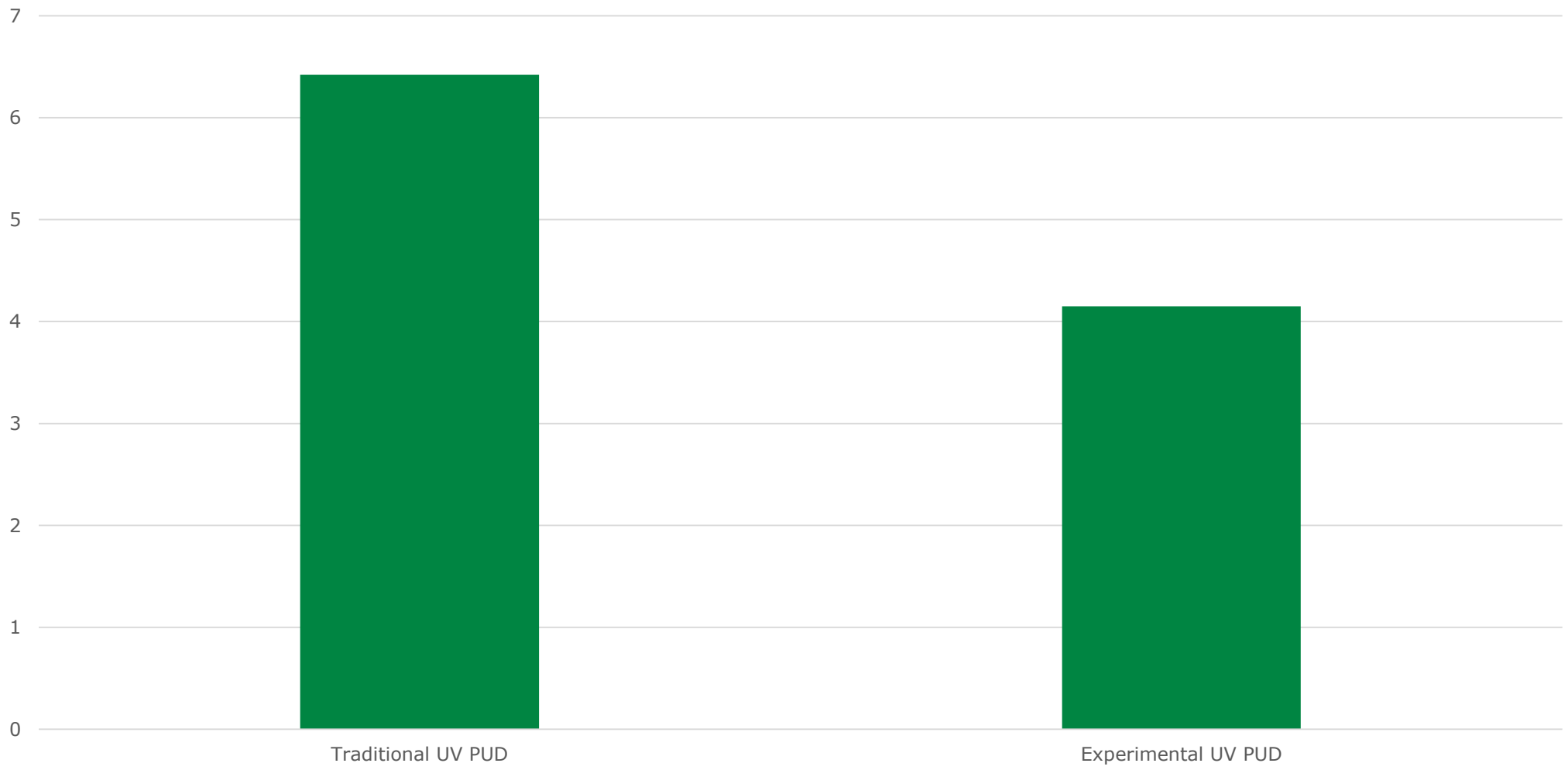
Chemical Resistance 16-hour spot test



Boiling Water Resistance



Scotch Brite Scratch Resistance - % Gloss Loss



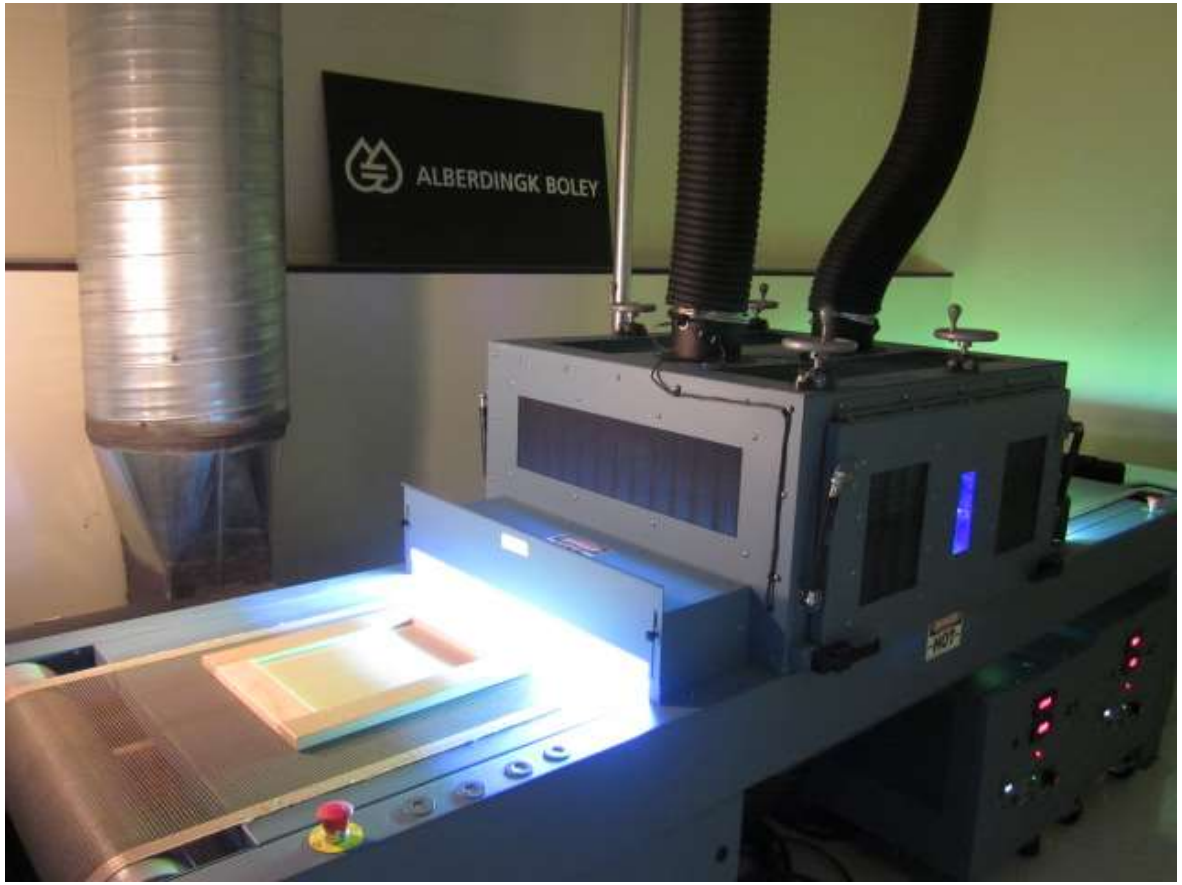
Elevated Temperature Stability – 50°C

	Traditional UV PUD	Experimental UV PUD
Initial Viscosity (cps)	142.5	16
Viscosity after 7 days	130.1	16
Viscosity after 14 days	68.5	17.5
Viscosity after 21 days	2360	15.5
Viscosity after 30 days	gelled	16

	Traditional UV PUD	Experimental UV PUD
Initial pH	6.99	6.92
pH after 7 days	6.51	6.93
pH after 14 days	6.06	6.83
pH after 21 days	5.54	6.39
pH after 30 days	gelled	6.26

Conclusions

The experimental UV PUD has equal performance to the traditional UV PUD but has superior elevated temperature stability.



Amine-free PUDs

Uses ammonia as neutralizing agent

High surface hardness

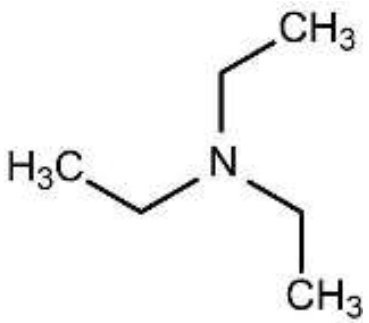
Very good chemical resistance

Suitable for wood floor and furniture coatings

Ideal for crosslinking with carbodiimides and silanes. The use of polyisocyanate is not recommended due to very high reactivity.

Amine-free PUDs
Background: The case for amine free

- Triethyl amine (TEA) is the most common neutralization agent for PUDs.



- According to GHS labeling it is flammable, harmful and toxic to the skin and eyes.

- Due to this classification, resulting binders and paints with TEA >1% have classification:

- TEA has a significant impact on emissions and indoor air quality.

Experimental

An amine-free PUD has been evaluated for use in KCMA/Furniture applications. Performance has been benchmarked against a traditional PUD and evaluated for:

Chemical resistance

Boiling water resistance – 1 hour

Scrape adhesion

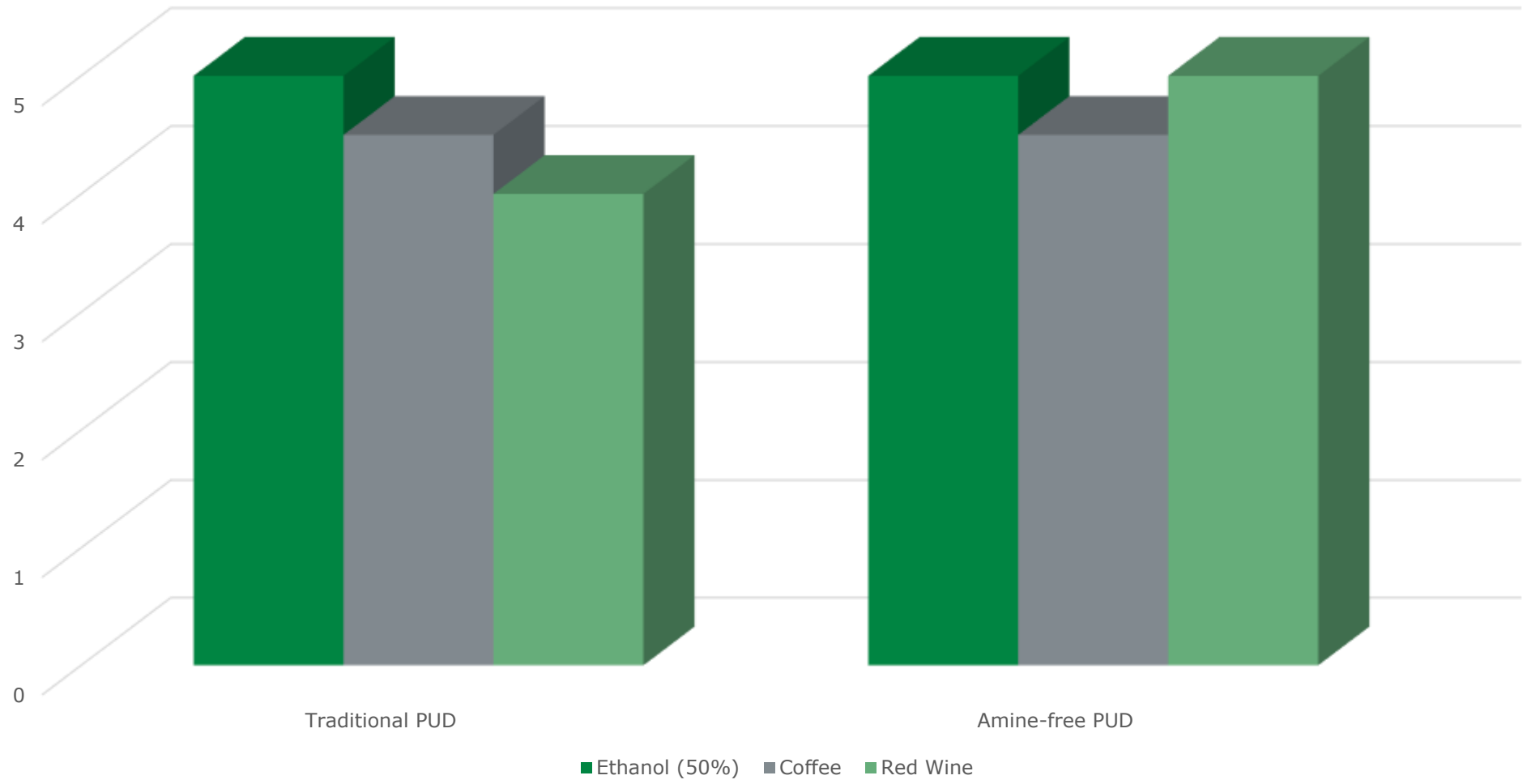
Taber Abrasion

Edge soak

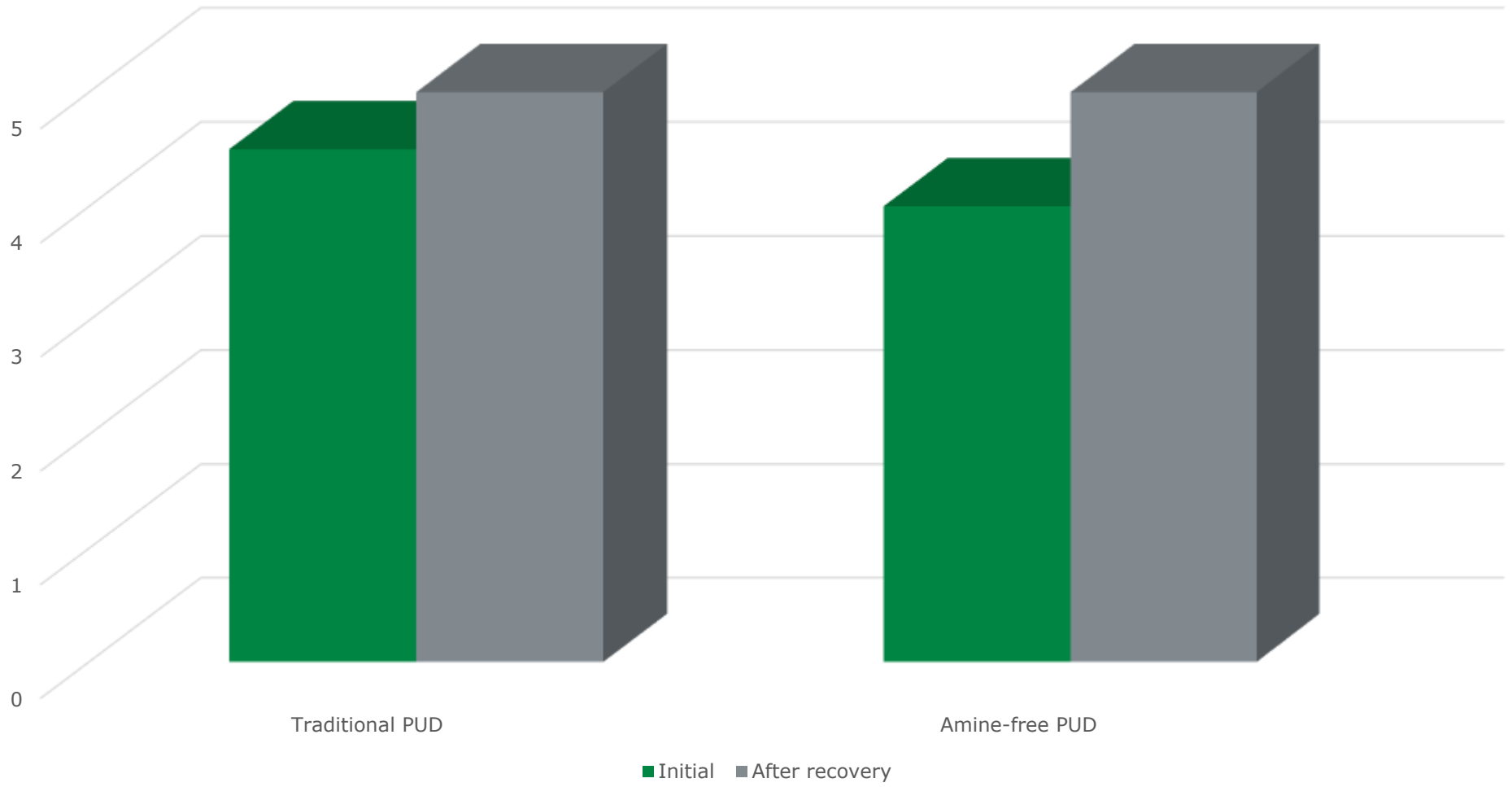
Wood Tone

Block resistance

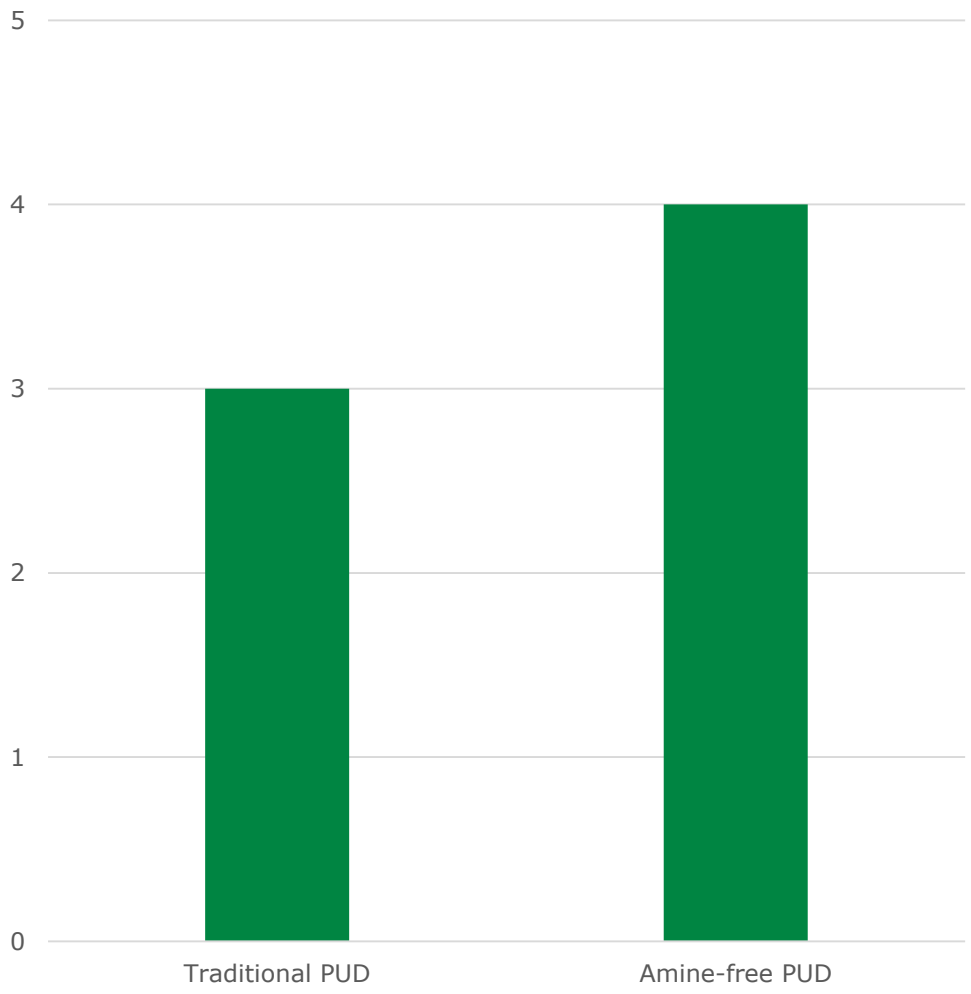
Chemical/Stain Resistance – 16 hour spot test



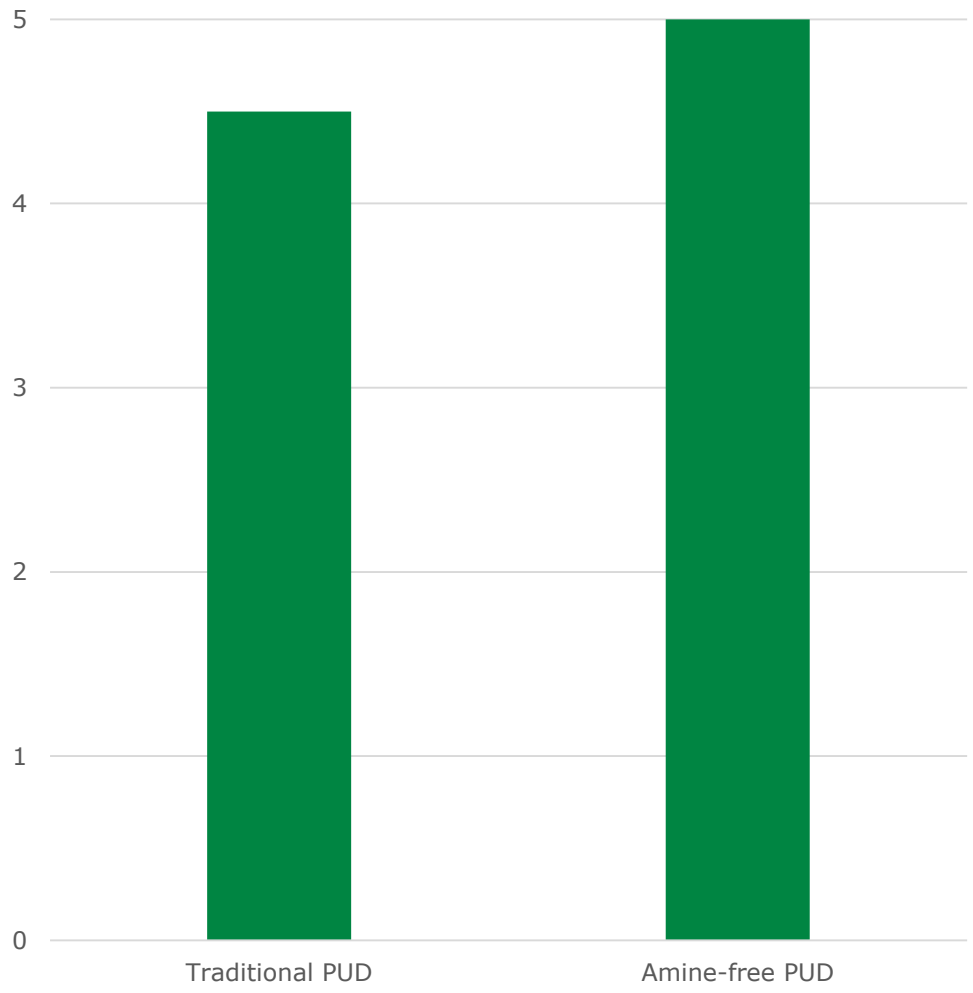
Mustard Resistance – 1 hour spot test

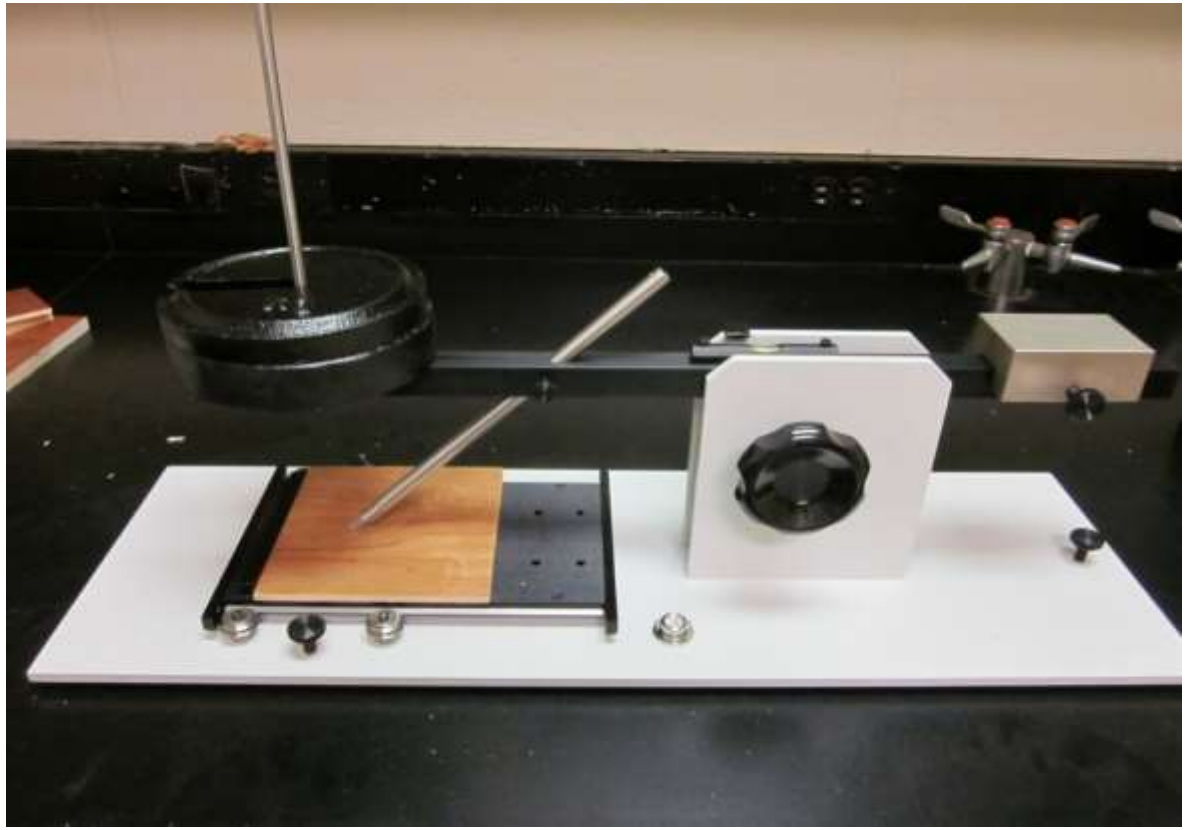


NEMA Boiling Water Resistance



BYK Balanced Beam Scrape Adhesion and Mar Tester – 5 Kg

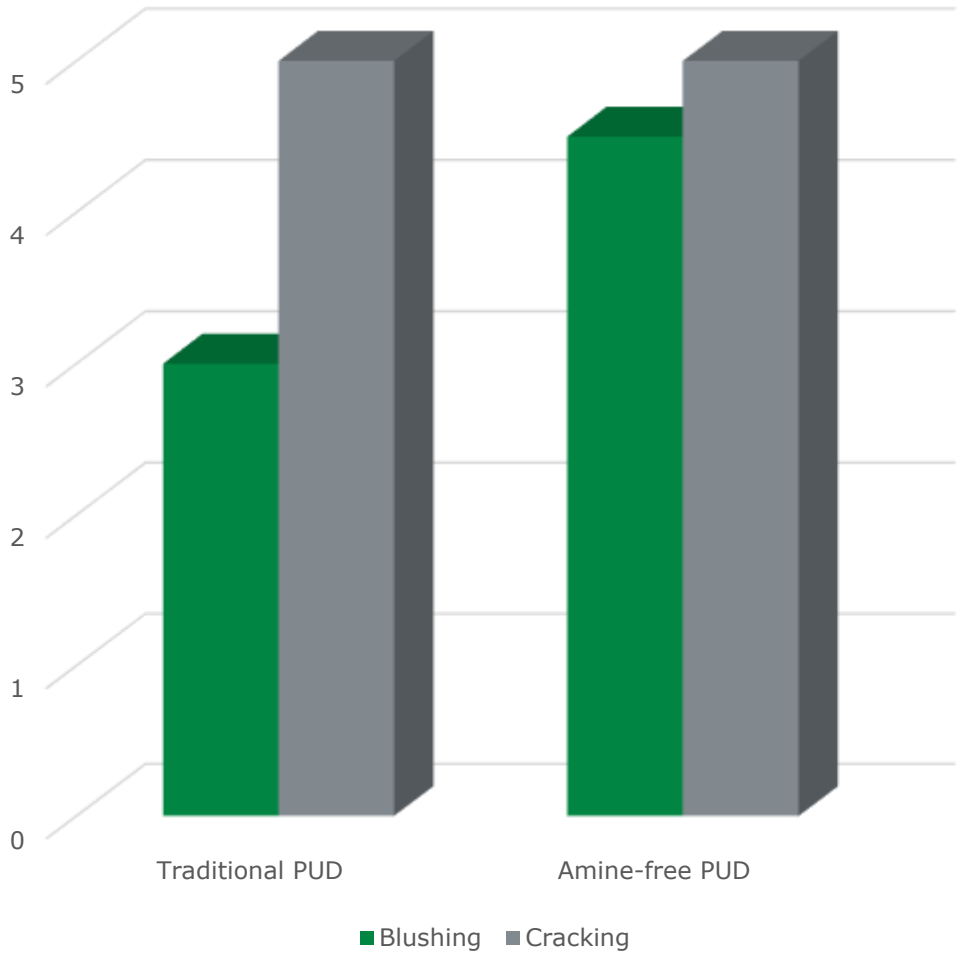




Edge Soak

Application:

Spray sealer coat @ 4 – 5 wet mils on solid red oak; air dry 1 hour and sand; spray topcoat at 4 – 5 wet mils; air dry 15 minutes; force dry 15 minutes at 50C; age 7 days. Place finished end grain area on sponge soaked in 1% detergent solution for 16 hours. Allow to recover for 4 – 8 hours. Examine for blushing and cracking.

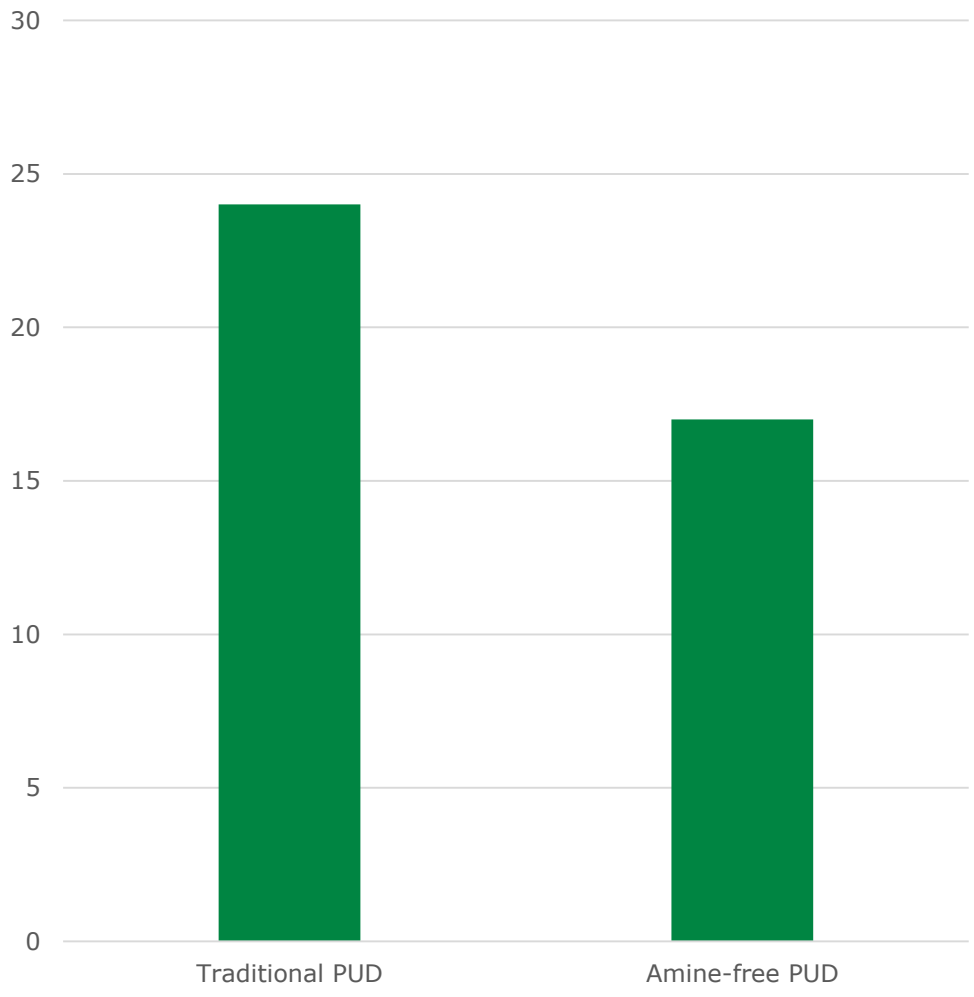


Taber Abrasion Resistance – 1000 grams; 1000 cycles; CS 17 wheels

Application:

6.0 Bird draw down on black scrub paper; air dry.

Age 7 days to test.



Conclusions

The amine-free PUD has excellent ethanol, Taber abrasion and water resistance.

It has excellent wood warmth and it atomizes and builds well.

The amine-free PUD is an excellent candidate for a KCMA and/or furniture coating.

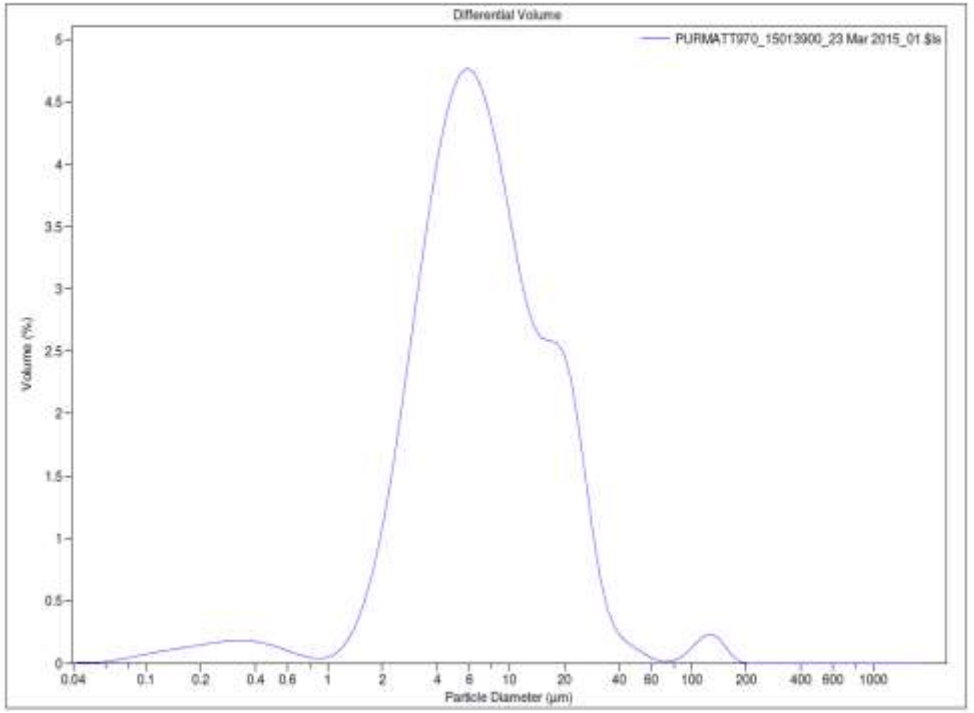
Inherently Matte PUDs

- High optical clarity on dark surfaces
- Hard but flexible film
- Anti-slip properties
- Excellent sandability
- Very good chemical resistance
- Very good blocking resistance

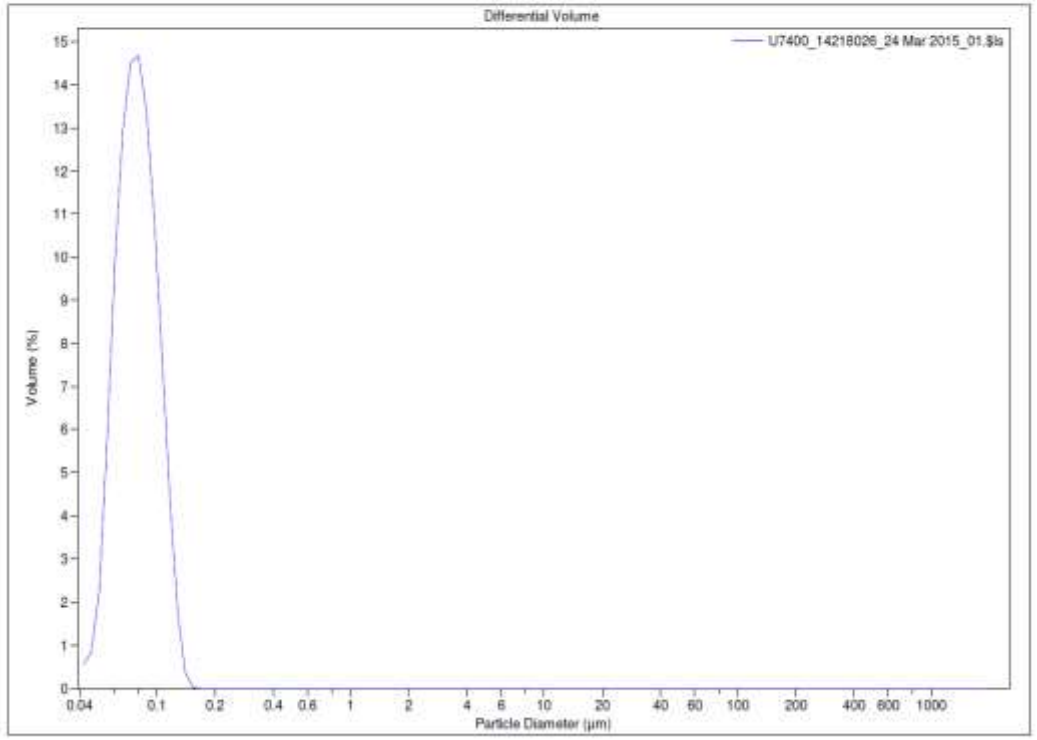
PUD w/2% silica Inherently matte PUD

Particle Size Distribution

Matte PUD

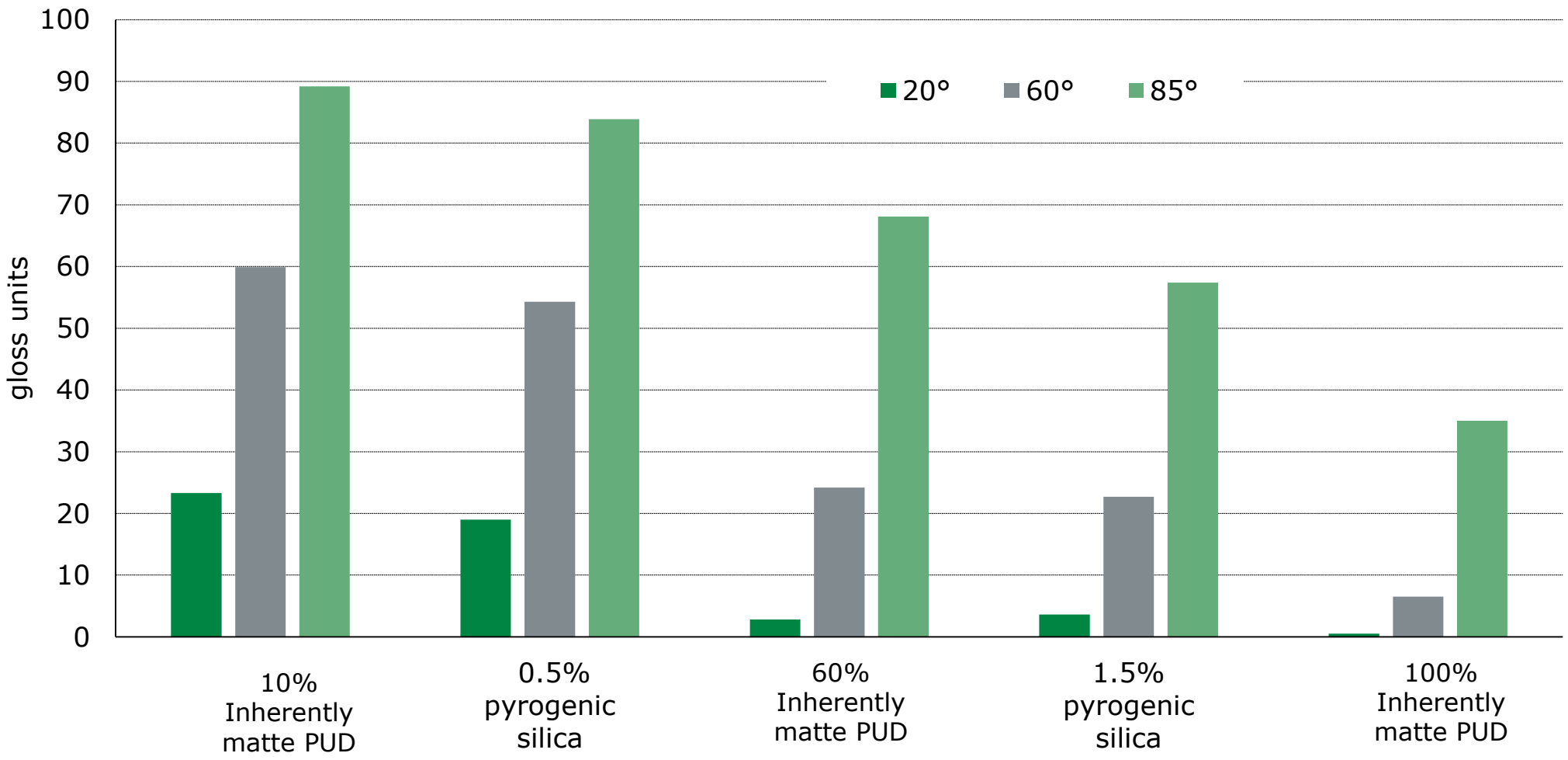


Standard PUD

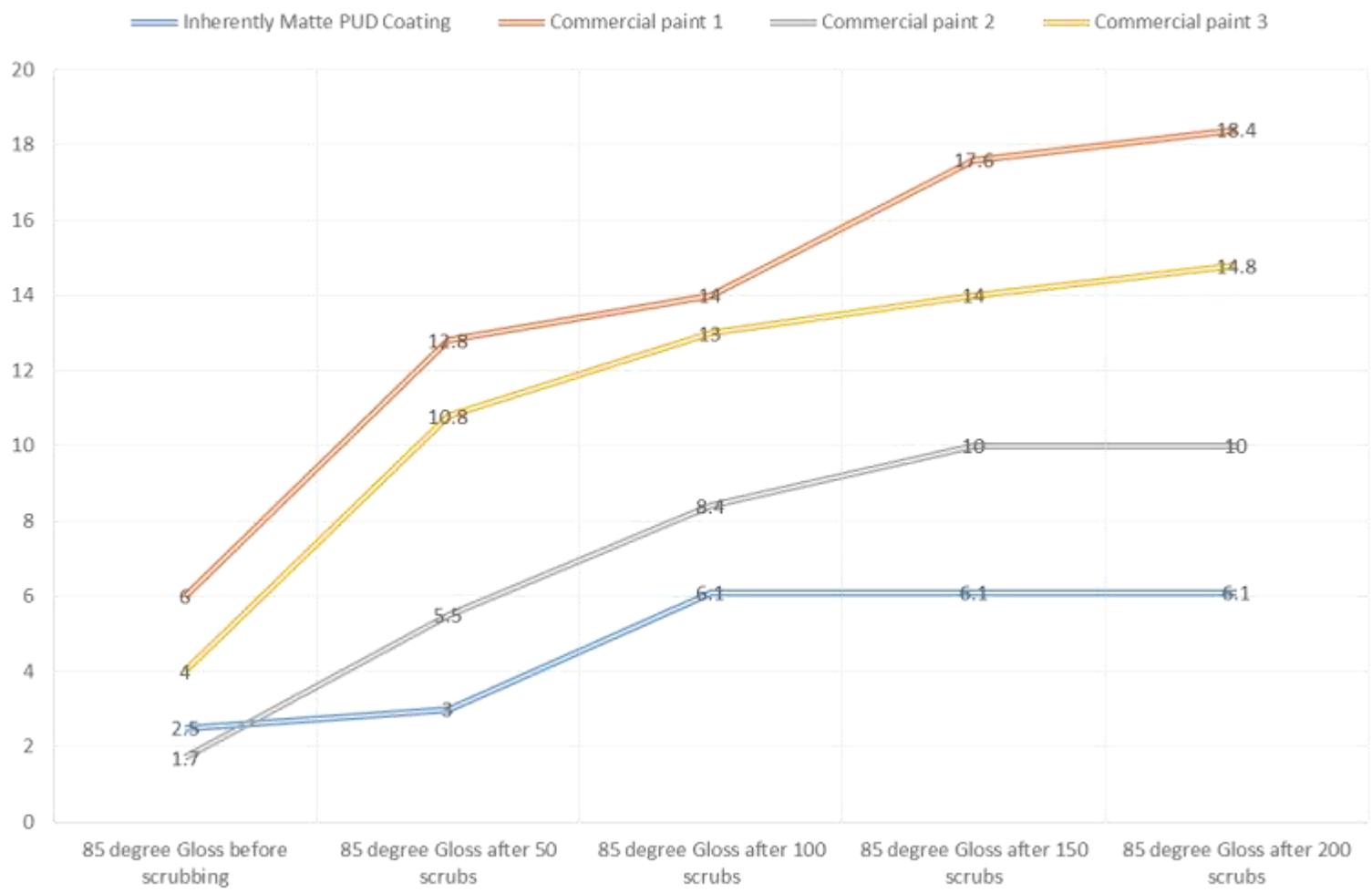


Particle size and particle shape can be controlled which influences haptic properties and gloss level

Matting efficiency vs. pyrogenic silica in traditional PUD



Gloss After Scrubbing – Burnish Resistance



Applications for Polyurethane Dispersions

Kitchen Cabinets and Office Furniture Coatings

Hardwood Floor Coatings

Exterior Wood Coatings

Textile and Leather Coatings

Architectural Wall Paints

Industrial Spray Lines (Cabinetry)

PUDs for Hardwood Flooring

Polyurethanes are the dominant choice for wood floors due to their flexibility, toughness and chemical resistance.

Solvent-based (1K oil modified) and Water-based (1K & 2K) materials are available in the market.

The Maple Flooring Manufacturer's Association (MFMA) is the authoritative source of technical and general information about maple flooring and related sports flooring systems.

M F M A
Maple Flooring Manufacturers Association, Inc.
The Sports Flooring Authority

Experimental

Several PUD types have been evaluated as 1K floor coatings according to the testing protocol of the MFMA.

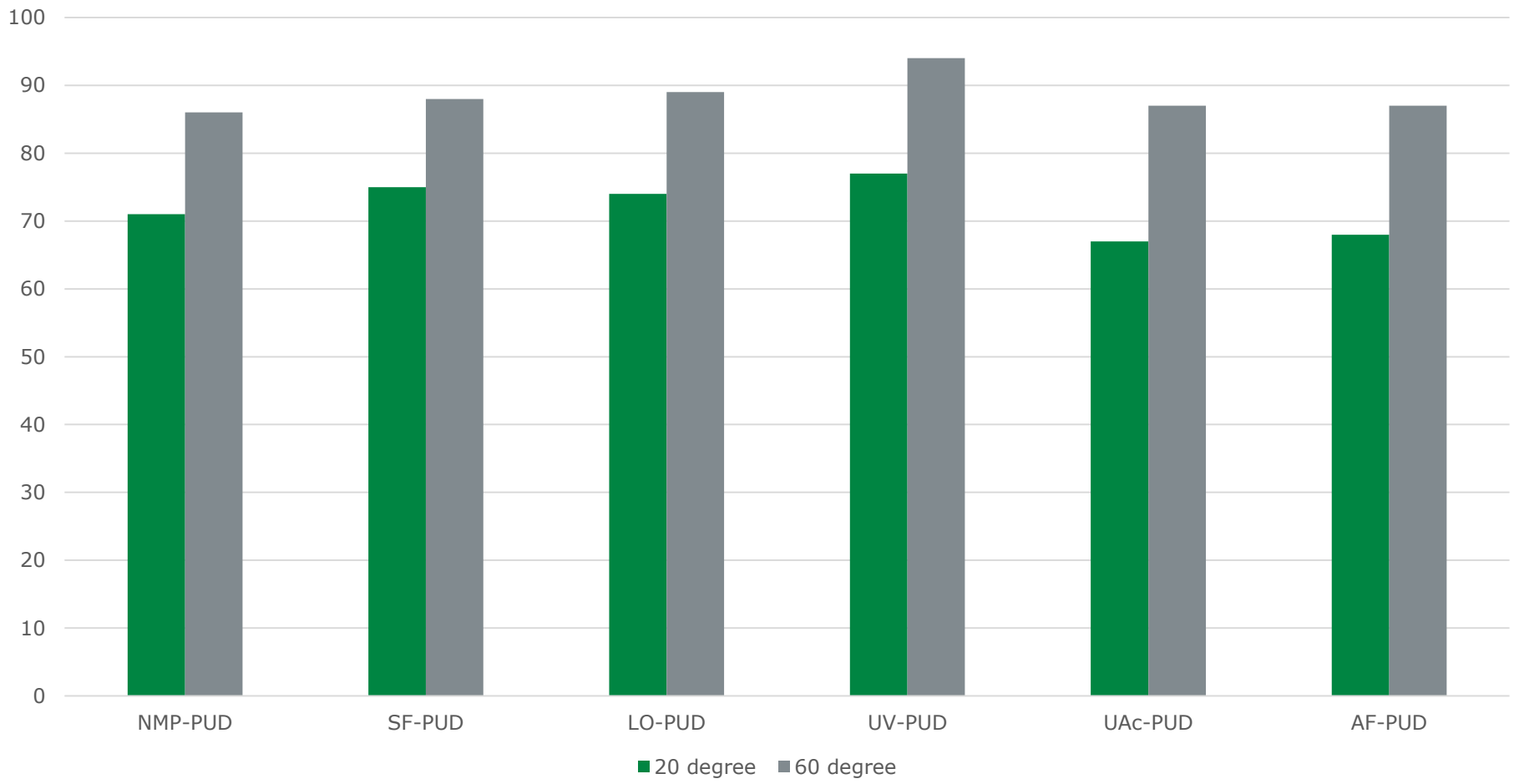
PUDs Evaluated:

- NMP Containing PUD
- Solvent-free PUD
- Linseed Oil Based PUD
- UV PUD
- Acrylic PUD Copolymer
- Amine-free PUD

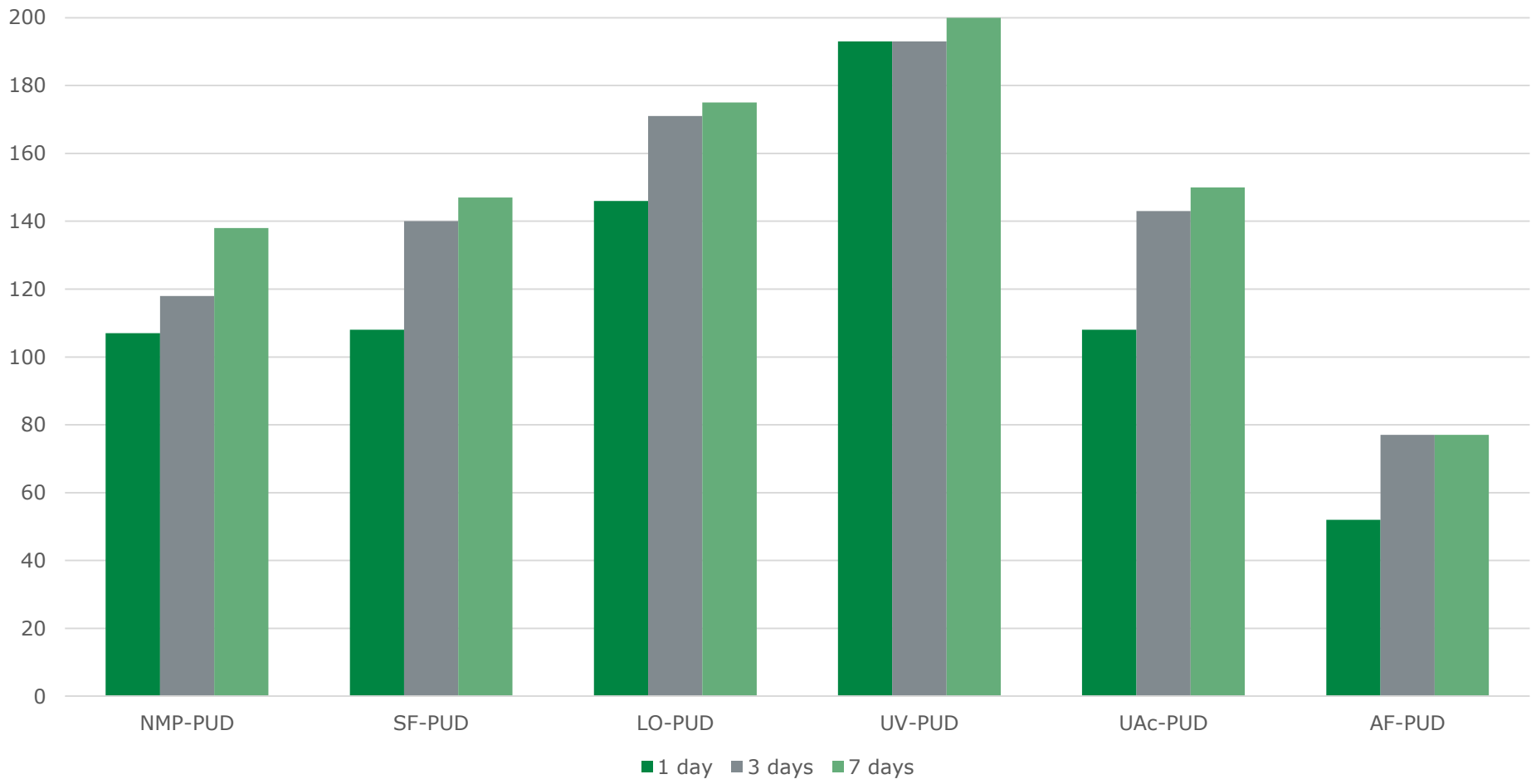
Performance Criteria:

- Gloss
- Hardness
- Black Heel Mark Resistance
- Chemical Resistance
- Taber Abrasion
- Coefficient of Friction (CoF)

Gloss

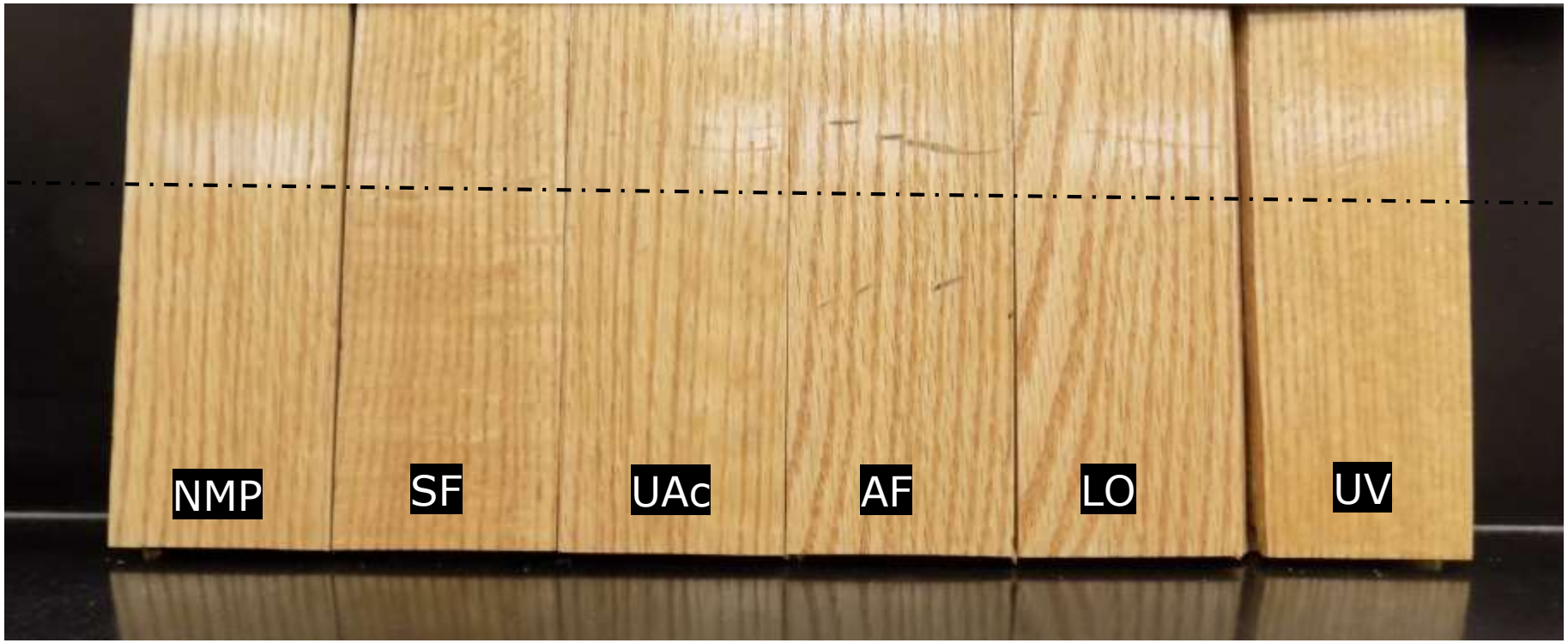

100
90
80
70
60
50
40
30
20
10
0
NMP-PUD
SF-PUD
LO-PUD
UV-PUD
UAc-PUD
AF-PUD
20 degree
60 degree

Koenig Hardness Development



Taber Abrasion

Black Heel Mark Resistance



3 days

7 days

Chemical/Stain Resistance (1h spot test)

	NMP	SF	UAc	AF	LO	UV
Red wine	2	3	4.5	5	4.5	5
Deonized water	5	5	5	5	5	5
Cleaning solution	5	5	5	5	5	5
Vegetable oil	5	5	5	5	5	5
Naphtha	5	5	5	5	5	5
Beer	5	5	5	5	5	5
Cola	5	5	5	5	5	5
Coffee	3	3	2	4	4.5	5
Ketchup	5	5	5	5	5	5
Mustard	2	2	2	2	3	5
Olive oil	5	5	5	5	5	5
70 % IPA	4	4	4.5	0	1	5
50 % Ethanol	5	5	5	5	5	5
Acetone	5	5	3	4	1	5
5 % Ammonia	5	5	5	5	5	5
Fantastic	5	5	5	5	5	5
Formula 409	5	5	5	5	5	5
	76	77	76	75	74	85

Rating: 0 – 5; 5 = best

Conclusions

All formulations resulted in high gloss coatings.

The UV PUD had the highest hardness values followed closely by the linseed oil-based PUD.

Taber abrasion of all coatings was excellent.

Black heel mark resistance was very good in all coatings except the amine-free product.

Chemical resistance was good in all coatings with the UV PUD being superior.

PUDs for Flexible Substrates – Textile and Leather Coatings

Features:
Extreme Flexibility
Hydrolysis Resistance
Non-Yellowing
Cold Resistance
Chemical Resistance
Light Fastness
Abrasion Resistance

Recommended Applications:
Automotive Leather
Automotive Interior Plastics
Synthetic Leather
Textile Coatings

Conclusions

- PUDs are one of the dominant resin technologies used to coat multiple substrates.
- Advances in PUD technology have resulted in a wide range of compositions offering unique performance to meet application requirements.
- PUDs can be blended with other waterborne technologies (acrylics, alkyds…) to enhance performance.
- PUDs are viable alternatives to traditional solvent-borne coatings.

Questions?

Laurie Morris

Senior Applications Chemist

Alberdingk Boley, Inc.

Office Phone: (336) 821-5531

Cell Phone: (336) 255-7243

lmorris@alberdingkusa.com